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SUPERCONDUCTIVITY

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SUPERCONDUCTIVITY

by

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GENERAL PREFACE

is the aim of these tracts to provide authoritative accounts of ıbjects of topical physical interest written by those actively ngaged in research. Each author is encouraged to adopt an ıdividualistic outlook and to write the tract from his own point of iew without necessarily making it "complete" by the inclusion of eferences to all other workers or to all allied subjects; it is hoped hat the tracts may present such surveys of subjects as the authors night give in a short course of specialised lectures.

By this means readers will be provided with accounts of those ubjects which are advancing so rapidly that a full-length book vould be out of place. From time to time it is hoped to issue ıew editions of tracts dealing with subjects in which the advance s more rapid.

M. L. O.
J. A. R.

CONTENTS

PREFACE

During the last few years, particularly since 1933, research on superconductivity has taken rather a new turn; previously it had always been tacitly assumed that the only essential feature of the superconducting state was infinite conductivity, and that the magnetic behaviour was a secondary feature which could be predicted from this property alone. The now classic experiment of Meissner and Ochsenfeld showed, however, that the predictions were sometimes quite wrong, and this discovery, together with the results of the recent work arising out of it, has led to a considerable revision of the phenomenological aspect of superconductivity, and has made more intelligible the fact that this change is not appreciably reflected except in the electrical and magnetic properties of the metal.

At the time when Kamerlingh Onnes first discovered superconductivity—1911—no proper theory of metals existed, and it was not surprising that this new phenomenon also could not be explained; since then, however, although wave-mechanics has found a satisfactory qualitative explanation for most metallic phenomena, superconductivity has remained as anomalous as ever from the theoretical point of view. The recent developments have not materially changed this position, but their importance is that they have at least made possible a coherent statement of what it is that the theory has to explain. This statement we have attempted to set out in the present survey.

Although the survey has been written mainly from the point of view of the recent developments, showing how it has become possible to correlate some of the properties of superconductors and thus to distinguish between fundamental and secondary features, it is intended also as a fairly comprehensive summary of superconductive phenomena in general. In describing the various experimental results, our aim has been to make clear the

essential principles involved, rather than the details of the methods by which the results have been obtained; similarly, to avoid confusing the main issues, no numerical data have been introduced into the text except for illustrative purposes, but these data are collected instead in an appendix for reference.

I wish to thank Prof. Landau for introducing me to many new ideas about the intermediate state (some as yet unpublished), to the idea that the zero resistance of a superconductor is a consequence of an exactly zero induction, and to the simple thermodynamical treatment of Chapter VI, and also for much detailed criticism which exposed (and removed) a number of theoretical prejudices originally held. I should like also to thank Dr Alexeevski, Dr Mendelssohn, Dr Misener, Dr Pomerantchuk and Prof. Shalnikov for their kindness in communicating details of their various researches in advance of publication, and allowing me to quote from their communications.

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Chapter I

INTRODUCTION—SOME ESSENTIAL FACTS

It was known a long time ago that the resistance of all metals decreases with temperature, the exact curve of decrease depending of course on the particular metal concerned, but in general following a course of the type shown in fig. 1 [1]. Matthiessen first pointed out that the resistance could be considered as made up of two parts: (i) a temperature independent residual resistance ΔR, which increased with mechanical strains in the specimen and with chemical impurity content, and (ii) a temperature dependent "ideal resistance", not appreciably affected by strains or impurities. The work of Kamerlingh Onnes in Leiden showed that already in the liquid hydrogen range of temperatures this ideal resistance was very small, so that most of the resistance was "residual", and independent of temperature. Soon after he had succeeded in liquefying helium, Kamerlingh Onnes began to extend his measurements into this new range of low temperatures, to see if this independence of temperature continued still closer to the absolute zero. For some metals this proved indeed to be the case, but in 1911 he found, quite unexpectedly, that the resistance of mercury suddenly disappeared when the temperature was reduced below a 4·16° K. certain point, no further change occurring at still lower temperatures (this behaviour is indicated by the broken curve in fig. 1) [2]. It seemed in fact as if the absence of resistance below the transition temperature

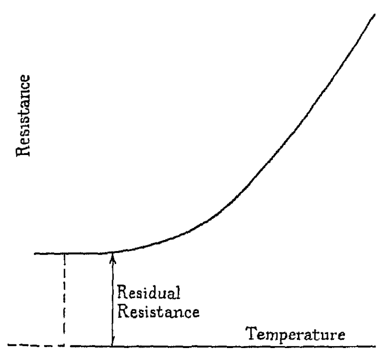

Fig. 1. Schematic resistance-temperature curve for a metal.

was characteristic of a new state of the metal—the "superconducting state".

This discovery opened up a whole series of problems about the scope and nature of the new phenomenon. As regards the scope of superconductivity, it has been found that seventeen metallic elements and a large number of alloys become superconducting, the transition temperature being characteristic of the particular metal, and varying from as low as 0·35° K. for hafnium up to 9·2° K. for niobium (certain alloys have slightly higher threshold temperatures). The known superconducting elements fall roughly into two groups in the periodic system (see Appendix, Table I), which suggests that superconductivity is probably not a universal property; but since every new advance in lowering of temperature* has revealed new superconductors, we cannot yet be certain that superconductivity is indeed limited only to certain metals. Since it is impossible to reach the absolute zero, this question can be definitely settled only by the development of a theory of the origin of superconductivity; unless, of course, further advances in lowering temperature should show that *all* metals do indeed become superconducting.

Attempts have been made to associate superconductivity with some other property of the metal, but so far most suggested empirical rules of this kind have broken down with the discovery of new superconductors (except perhaps the rule suggested above, that superconductivity is confined to certain groups of the periodic system). For instance, it was thought that only "soft" metals with low melting points became superconducting, until it was found that the typical "hard" metals tantalum and niobium also became superconducting, and moreover with relatively high transition temperatures. Similarly, no particular type of crystal lattice seems to be necessary for superconductivity, since nearly all the types are represented in the list of known

* For instance the recent work of Kürti and Simon (3) with the adiabatic demagnetization technique.

superconductors. By this we do not, of course, mean to imply that the crystal lattice is of less importance than the atomic species of the metal, for just as with ordinary conductivity, any change of crystal lattice for a metal of given atomic species can have a profound effect. This is strikingly illustrated by the case of tin, the only superconductor with more than one modification. Thus white tin is a typical superconductor, while grey tin, which differs from it only in its crystal lattice, does not become superconducting down to the lowest temperature tried (2·3° K.) (4).

An important question as to the nature of superconductivity was to decide whether it was the whole, or only a part, of the resistance which disappeared in the transition to superconductivity, for it was sometimes suggested that only the residual resistance vanished, leaving the ideal resistance, which was too small to be observed in Kamerlingh Onnes' experiment. This question was only settled by later experiments (5), using the indirect method of looking for a decrease of a "persistent" current in a superconducting ring (see Chapter IV). These experiments showed that the upper limit of any possible resistance in the superconducting state was less than $10^{-15}R_0$, where R_0 is the resistance at room temperature; and since the ideal resistance just above the threshold temperature is certainly much greater (of the order $10^{-8}R_0$), we see that it must be the total, and not merely the residual resistance, which disappears. In fact no experiment so far has revealed any trace of resistance in a superconducting metal, and we shall always assume in what follows that a superconductor behaves as if its resistance were actually zero. This is equivalent to saying that the component of the electric field E in the direction of the current flow is zero, and since there is no evidence for a non-zero component in any other direction,* we can say that $E=0$ is an essential property of a superconductor.

Presumably the complete and abrupt loss of resistance must

* There is, for instance, no Hall effect in a superconductor (6).

be a consequence of some more fundamental change in the electronic or atomic structure of the metal, and the experiments to elucidate the nature of this change can be divided roughly into two classes: (*a*) those to test whether this change is reflected in any properties of the metal other than its resistance, and (*b*) those to test whether the change can be affected in any way (e.g. inhibited or encouraged) by various physical agents.

For a long time one of the most baffling features of superconductivity was that all the experiments of the type (*a*) gave negative results, or, in other words, that apart from the loss of resistance the metal appeared to have identical properties both in the superconducting and normal states. More recent experiments have revealed some exceptions, and at the same time thermodynamical considerations have, as we shall see later, made the lack of change of properties in the superconducting transition more understandable. It is convenient to list here the various properties which have so far been investigated with negative results.

(1) The X-ray diffraction pattern is the same both above and below the transition temperature (**7**), which shows that no change of the crystal lattice is involved. The absence of any appreciable change in the intensity distribution also shows that the change in the electronic structure must be very slight.*

(2) There is no appreciable change in the reflectivity of the metal either in the visible or the infra-red region (**8**), although the optical properties are usually closely connected with the electrical conductivity.

(3) There is no change in the absorption of fast or slow electrons (**9**), and the photoelectric properties are also unchanged (**10**).

(4) In the absence of a magnetic field there is no latent heat

* Debye (**7a**) has suggested a method, based on a study of a continuous background of the X-ray diffraction picture, by which such a slight change in the electronic structure might be detected. Scharwächter (**7b**) has applied the method to study the electronic structure of beryllium, but it has not yet been applied to any superconductor.

at the transition (11). We shall see later that this is connected thermodynamically with the magnetic properties (Chapter v).

(5) The elastic properties (12) and the thermal expansion (13) are the same in the superconducting and normal states, and there is no appreciable change of volume in the transition (13).

The exceptions mentioned above (i.e. the properties which do change in the transition to superconductivity) are the following:

(1) The magnetic properties undergo a change no less remarkable than that of the electrical properties: this change will be discussed in detail in the following chapters.

(2) The specific heat changes discontinuously at the transition temperature (11), and in the presence of a magnetic field there is also a latent heat of transition (14). These features find a detailed explanation in the thermodynamic treatment (Chapter v).

(3) All the thermoelectric effects disappear when a metal becomes superconductive (15).* Landau (unpublished) has suggested that this is probably a simple consequence of the absence of resistance in the superconducting state, and is thus not an independent feature. The argument for this assertion is of a nature similar to that by which the absence of resistance is deduced from the magnetic properties (see Chapter II), but it has not yet been fully developed.

(4) The thermal conductivity in a magnetic field changes discontinuously at the transition temperature, though its order of magnitude remains the same. It becomes lower in the superconducting state in the case of a pure metal, but higher in the

* Keesom and Matthijs (15) find that although the thermoelectric power vanishes below the transition temperature, its disappearance is not abrupt, but spread over a temperature range of 1 or 2° K., in which the thermoelectric power in general increases with the strength of an applied magnetic field; corresponding to this, the Thomson effect shows a marked maximum just above the transition temperature. Whether these effects really indicate, as Keesom and Matthijs suggest, a continuation of some feature of the superconducting state above the threshold temperature, or whether they are due to "non-ideal" conditions (e.g. impurities), is not yet clear. We are inclined to the latter explanation, since in ideal conditions all other effects which change in the superconducting transition do so discontinuously, and it has generally been found possible to ascribe experimentally found gradual changes to secondary features.

case of an alloy. In the absence of a magnetic field there is no discontinuity (16). These phenomena will probably be understood only when we have an electronic theory of superconductivity.

We now turn to the results of experiments of type (*b*). The influence of high-frequency radiations, such as X-rays, and of electrons and α-rays, does not appear to have been studied, but it is unlikely that they should have any effect, since the processes associated with their passage through the metal in general involve only single electrons or atoms, while conductivity is always a phenomenon involving the collective behaviour of many electrons.

The effect of increasing the frequency of the current in a superconductor has been investigated by McLennan and his collaborators (17) up to radio frequencies, but although their experiments suggested that the transition temperature began to fall off at the highest frequencies used (10^7 c./sec.) the effect was very small and might have been due to some secondary cause, so that we may say that there is no appreciable influence of frequency on the transition temperature up to 10^7 c./sec. We shall see in Chapter II that an essential property of a superconductor is that a magnetic field cannot enter it, unless the field is greater than the "critical" field (see below), and it follows that there should be no absorption of energy by a superconductor in an alternating magnetic field, unless the frequency is high enough to affect the superconducting property. This has been investigated up to frequencies of the order $5 \cdot 10^7$ c./sec. (18) and no absorption has indeed been found, thus confirming McLennan's result that superconductivity is not affected by increase of frequency up to 10^7 c./sec. The question of the order of magnitude of the frequency at which energy absorption might be expected to occur will be discussed in Chapter VIII.

The transition temperature can be changed by a stress; if the stress increases the dimensions, the transition temperature is increased (19). This effect is, however, only very slight, presumably because the change of dimensions caused by any

practicable stress is also very small. Associated with this effect there is also a slight influence of stress on the critical magnetic field at a given temperature. In Chapter V we shall show that the lack of any appreciable change in the thermal expansion, the compressibility, and the volume of the metal in the superconducting transition, is connected thermodynamically with the small magnitude of the effect of a stress on the superconducting properties.

Reduction of the size of the specimen below about 10^{-4} cm. modifies the superconducting properties in many important respects. It is more convenient to discuss these effects later (Chapter VII), after we have dealt with the properties of superconductors of normal dimensions.

The most important effect of a physical agent at present known is that of a magnetic field. If a magnetic field is applied parallel to the length of a long superconducting wire, the resistance of the wire is suddenly restored at a definite field strength, which depends on the temperature, and is characteristic of the particular metal concerned; this field is known as the "critical field" (20). The restoration of resistance is, however, abrupt only if the metal is perfectly pure and free from strains and if the current used for measuring the resistance is vanishingly small. The absence of impurities and strains is important because these slightly change the critical field, and consequently different regions of the specimen may have different critical fields if impurities or strains are present, so that the transition is blurred. The influence of the measuring current, and the necessity for the particular geometrical conditions specified above, will be explained later. We may say, then, that a lack of sharpness in the restoration of resistance by a magnetic field at a given temperature (or what is equivalent, by an increase of temperature at a given field—which may in particular be zero) is in general a secondary feature, and in our treatment we shall assume that the conditions are ideal, and that there is a perfectly definite critical field at a given temperature.

We should mention also, that if these ideal conditions are fulfilled—and they have been closely approached in practice—the transition from super to normal conductivity is a reversible one, i.e. if the field is reduced from a value above the critical, the resistance disappears at the same field strength as that for which it appeared in increasing fields. Actually, in many of the early Leiden experiments, complicated hysteresis effects were found in the resistance-field curves, but these were greatly reduced when the potential leads to the specimen were welded instead of soldered (21), which suggests that the hysteresis was of secondary origin, probably connected with the anomalous properties of alloys (Chapter VI).*

The relation between the critical field H_c and the temperature is of great importance for characterizing the properties of any particular superconductor. The detailed form of this relation is different for different superconductors, but in its general features it can be represented by a curve such as that of fig. 2. The detailed curves for the actual superconductors will be found in the Appendix (fig. 23) and it may be noticed that the curves fall roughly into two groups, which seem to correspond to the two groups of superconductors in the periodic system: the "hard" superconductors of the left-hand group have very

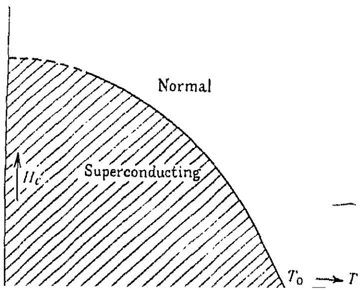

Fig. 2. Schematic H_c-T diagram.

* The hysteresis may have been in part due to impurities in the specimen, for, as we shall see in Chapter VI, superconducting alloys show marked hysteresis effects, but in certain cases the hysteresis was of a type rather different from that characteristic of alloys or impure specimens, and may have been due to some sort of "supercooling" (see p. 39). Although in our discussion of pure superconductors we shall suppose that the hysteresis effects are always of secondary origin, and so need not be taken into account, the position is not entirely cleared up from the experimental point of view, and it is just possible (though we think unlikely) that our supposition is not completely permissible.

steep H_c-T curves, while the "soft" ones of the right-hand group have much less steep curves. It is not certain, however, whether this rule is of general validity, since not all the superconductors have been investigated—in this connection measurements on vanadium and titanium would be of interest. It is often convenient to think of the H_c-T curve as an equilibrium diagram, in many ways analogous to the p-T diagram for an ordinary phase transition such as melting or boiling; thus states of the metal falling in the shaded region are superconducting, while other states are normally conducting. Close to the normal transition temperature (i.e. that in field zero), this threshold curve is approximately parabolic and can be represented roughly by the formula $H_c = a(T_0^2 - T^2)$. The curve meets the T-axis at an acute angle, and becomes flat as we approach absolute zero, in accordance with Nernst's theorem which, as we shall see later, requires dH_c/dT to vanish at $T=0$. The order of magnitude of the maximum critical field is from 100 to 1000 gauss for the known superconductors.*

An interesting consequence of the existence of a critical magnetic field is that there is also a critical strength for the current flowing in a superconductor (22). The disturbance of superconductivity by a current was actually discovered before that by a magnetic field; it was revealed when Kamerlingh Onnes tried to produce high magnetic fields without power loss by means of a superconducting solenoid. As soon as the current exceeded a certain value, corresponding to only quite a small field in the solenoid, the resistance appeared again and the current could be maintained only with a great supply of energy. After the discovery of a critical magnetic field, Silsbee (23) pointed out that the effect of a current in restoring the resistance might be merely due to the magnetic field which it produced, and this

* It is just possible that superconductors exist with very much smaller critical fields, but not unduly low transition temperatures, and that their superconductivity has not been detected because the experiments did not sufficiently exclude small stray fields, such as that of the earth or of the measuring current.

hypothesis was later verified experimentally, which showed that the current effect is merely a secondary feature.

We have now mentioned most of the essential features and properties of pure superconductors,* and can go on to consider in more detail how they are related to each other, and to discuss the more recent results.

* The properties of alloy superconductors differ in several characteristic respects, but since these properties are probably in a sense secondary, it will be more convenient to deal with them in a separate chapter (Chapter VI).

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Chapter II

THE MAGNETIC PROPERTIES OF A PERFECT CONDUCTOR AND A SUPERCONDUCTOR

In this chapter we shall first of all show what magnetic properties could be expected for a metal in the limiting case of infinite conductivity, and then contrast these with the actual magnetic behaviour of a superconductor; this comparison will show that the description of a superconductor merely as a perfect conductor is clearly inadequate, and in a certain sense even incorrect.

Consider a metal of zero resistivity and unit permeability (i.e. $B=H$). Inside the metal we have the electrodynamic equations:

$$\text{curl } E = -\frac{1}{c}\frac{dB}{dt}, \tag{1}$$

$$\text{curl } H = 4\pi j/c; \tag{2}$$

also since the metal has zero resistance,

$$E = 0, \tag{3}$$

and so we see from (1) that $dB/dt=0$, or

$$H = B = H_0, \tag{4}$$

where H_0 is the field which was in the metal at the moment when it lost its resistance. It follows also from (2) that

$$j = \frac{c}{4\pi}\text{ curl } H_0 = j_0, \tag{5}$$

where j_0 is the current density which was in the metal when it lost its resistance; in particular if (as we shall assume in the rest of this chapter) there were no currents initially, there would be none inside the metal later, however the external field was varied. The physical meaning of these results is that any change of the external magnetic field induces currents on the *surface* of the metal, and the magnetic field of these currents inside the

metal just compensates the change of external field, thus keeping the field inside the metal constant. Since there is no resistance, the surface currents cannot die away and so the field inside the metal remains constant with time.

The strength of the surface currents is given by the discontinuity of the tangential component of the field in crossing the surface of the metal, i.e. the surface current density vector g is

$$g = \frac{c}{4\pi}(H_{\text{tang}} - H_{0\,\text{tang}}), \tag{6}$$

where H_{tang} and $H_{0\,\text{tang}}$ are the vectors which represent the components of H and H_0 in the surface.

The magnetic moment of the metal caused by these surface currents can be calculated by solving the field-distribution problem and then integrating the product of the current round each closed filament of the surface and the area of the filament, over all the filaments. A simpler procedure, however, is to take account of the magnetic effect of the induced currents by treating the superconductor as a magnetic body, i.e. by supposing that $H \neq B$. The induced currents then no longer appear explicitly, but are supposed to have a nature similar to that of the atomic currents responsible for ordinary magnetism—this, of course, is possible only because the induced currents do not vary with time in steady external conditions. The magnitude of the current density (which we still denote by j) is now given by

$$j = c/4\pi \text{ curl } B, \tag{7}$$

and since $B = H_0$, we deduce just as before that the currents must be entirely superficial (if there were no body currents originally present) and that the surface current density is given by equation (6). The field* H is the gradient of some potential ϕ, satisfying the equation $\nabla^2\phi = 0$, and ϕ and the tangential component of H must now be continuous across the surface (the

* The actual magnetic field in the metal is B and not H. The vector H is introduced really only as a mathematical device in the case when B is independent of the externally applied field, and has no direct physical meaning—this will be more fully explained in Chapter III.

surface current now being connected with the discontinuity of the tangential component of B); thus H can be determined by the usual mathematical methods. We then have that I, the magnetic moment per unit volume, is given by

$$B = H + 4\pi I. \tag{8}$$

This field-distribution problem, as is well known, can be solved exactly for an ellipsoid in a uniform field (i.e. if the field would be uniform in the absence of the specimen), and to illustrate the nature of the magnetic properties, we consider the simplest possible case—that of an infinitely long cylinder (the limiting case of an elongated ellipsoid) in a uniform field parallel to the axis of the cylinder. In this case the field distribution of H is not affected by the presence of the specimen, and so H is just equal to the external field. We thus have

$$I = -(H - H_0)/4\pi, \tag{9}$$

as long as the metal has zero resistivity, and we can construct the magnetization curve of the specimen shown in fig. 3 *a*. If the cylinder lost its resistance in zero field, then $H_0 = 0$, and

$$I = -H/4\pi,$$

i.e. the metal behaves like a diamagnetic substance of volume susceptibility $-1/4\pi$, or in other words of zero permeability. This continues until the critical field H_c is reached, when, as we saw in Chapter 1, the resistance reappears; the surface currents then die away and leave the body with no magnetic moment. If now the field is again reduced, the resistance again disappears as soon as $H < H_c$, but now $H_0 = H_c$, and the magnetization is given by

$$I = -(H - H_c)/4\pi. \tag{10}$$

We see therefore that there should be a very marked hysteresis effect, and that when the external field is zero, the cylinder should be left with a "frozen-in" paramagnetic moment $H_c/4\pi$ corresponding to the "frozen-in" flux, $B = H_c$. The physical meaning of this hysteresis is simply that for a reduction of the

field the surface currents are induced in a sense opposite to that for an increase of field; the area $ABCD$ is proportional to the energy lost irreversibly in the form of Joule heat when the surface currents die away at B.

If the metal is cooled in some field H_0, no magnetic moment should be observed at or below the temperature at which it loses its resistance, but if, after this temperature has been passed, the field is reduced, the magnetization will be given by equation (9), which in this case again represents a paramagnetic moment (corresponding to the section EF in fig. 3 a).

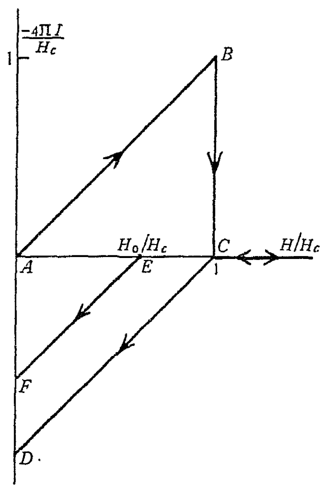

Fig. 3 a. Magnetization curves of a perfectly conducting long cylinder.

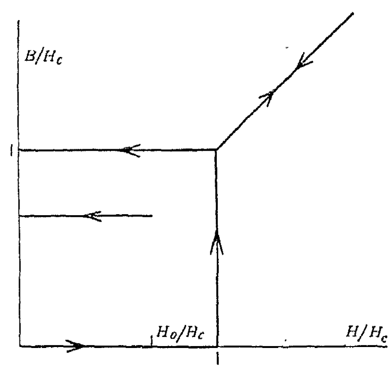

Fig. 3 b. B-H curves of a perfectly conducting long cylinder.

In fig. 3 b we show also the corresponding B-H curves for a perfect conductor, i.e. $B=H_0$ for $H<H_c$ and $B=H$ for $H>H_c$.

Until recently these predictions were generally regarded as so self-evident as not to require an experimental test, and in the literature on superconductivity frequent references to the supposed "frozen-in" moments can be found, although their

existence had never been shown experimentally. In the course of some experiments on the magnetic field distribution round superconductors, Meissner and Ochsenfeld (1) in 1933 first showed that some of the predictions for a perfect conductor were quite wrong for an actual superconductor. They found, in fact, that for a pure superconductor, the field distribution always corresponded to zero field inside the superconductor, or in other words that inside a superconductor we always have

$$B=0 \tag{11}$$

instead of $B=H_0$, independently of the initial conditions (i.e. of the field in which the metal became superconducting). Later experiments showed that this result was quite general, and not connected in any way with the particular experimental arrangement used by Meissner; let us see now what this "Meissner effect" means in our simple case of a long cylinder.

If the cylinder was cooled below the transition temperature in zero field, the magnetization will of course vary with a subsequent increase of field just as for a perfect conductor, i.e. $I=-H/4\pi$, and at the critical field the magnetization will as before disappear (this is simply because in this case $H_0=0$, and therefore $B=0$ is equivalent to the result $B=H_0$ for a perfect conductor). It is only on again reducing the field that the properties of the actual superconductor begin to differ from the predictions for a perfect conductor; thus according to Meissner's discovery no field can ever exist in a superconductor, and so when the field is reduced below H_c all the lines of force in the cylinder are suddenly pushed out, and the magnetization is again given by $I=-H/4\pi$, without any hysteresis. Similarly, if the metal is cooled in field H_0, as soon as the temperature reaches the critical value for this field, the lines of force are suddenly pushed out, and the cylinder acquires a magnetization $-H_0/4\pi$. In other words, the magnetization curve is always given by

$$I=-H/4\pi \tag{12}$$

independently of the initial conditions, as shown in fig. 4*a*, and

whatever the field in the body may have been just before it became superconducting, it is always zero in the superconducting state. Correspondingly, the *B-H* curve for the superconducting cylinder is as shown in fig. 4*b*, with *B* always zero in the superconducting state and $B = H$ in the normal state.

We have so far spoken as if the induction *B* were exactly zero in a superconducting metal, but this is of course rather more than can be deduced from the magnetic measurements, which could not exclude the interpretation that *B* was merely very small, but not zero. We shall show directly that if we assume

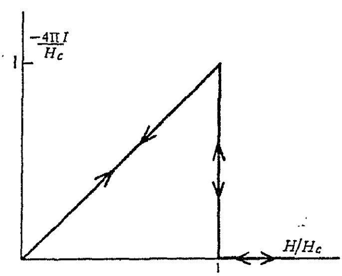

Fig. 4*a*. Magnetization curve of a superconducting long cylinder.

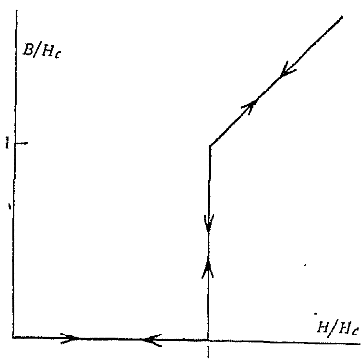

Fig. 4*b*. *B-H* curve of a superconducting long cylinder.

$B = 0$ is exactly true, it follows that $E = 0$, and since we know from the resistance measurements (and from the occurrence of persistent currents in a ring) that this is indeed so, it is natural to infer that *B* is really exactly zero in a superconductor, and not merely very small. The importance of this result is in showing that the essential property of a superconductor is its zero permeability rather than its zero resistance, but we must emphasize that the experimental verification of the zero resistance is necessary before we can deduce that *B* is not merely too small to be measured in the magnetic experiments, but really vanishes completely.

If we assume that B is indeed exactly zero inside the superconductor,* it follows at once that the total current density j must also vanish inside the superconductor, since $j = c/4\pi$ curl B. Since any electric field would produce a current in the metal, we conclude that E is also zero. This is not yet a sufficient justification for supposing that E vanishes *throughout* the superconductor, for in some very thin surface layer, there must certainly be non-vanishing values of B (this is of course the layer in which the surface currents flow), and it might be thought that E also did not vanish in this layer. This cannot be so, however, for from equation (1) it follows that in stationary conditions (i.e. $dB/dt = 0$) curl $E = 0$ in the layer as well as elsewhere in the metal, so that if E vanishes in the body of the metal it must vanish throughout.

The property $E = 0$ is of course just what was deduced from the absence of resistance in the superconducting state, but in order to show that the absence of resistance can really be deduced from $B = 0$ we have still to explain how it is possible for a "total" current to flow in the absence of an electric field. The surface currents responsible for the magnetism of an ordinary body with non-zero permeability μ can in fact never combine in such a way as to form any "total" current in the absence of an electric field, for if they did, it would be impossible to satisfy the conditions div $B = 0$ and curl $B = 0$ inside the specimen. Consider, for instance, a plate in a magnetic field everywhere parallel to the surface of the plate (see fig. 5), and suppose the surface density g_1 of current is greater going up one side than that (g_2)

* This treatment, on the basis of B exactly zero, is essentially equivalent to what can be obtained from the theory of F. and H. London (2) by putting their parameter Λ equal to zero (we should point out also that their H is what we call B). Our treatment of course makes no attempt to deal with the conditions in the surface layer, and applies only to bodies of size large compared with the thickness of this layer, but it should be noticed that the London theory is based on an arbitrary assumption as to the conditions in the surface layer. The truth of this assumption can be tested only by experiments on specimens of microscopic dimensions (i.e. of size comparable with the larger thickness), but such experiments (Chapter VII) do not as yet provide any definite evidence.

coming down the other, so that there is a total current $g_1 - g_2$ per unit width going up the plate. We should then have:

$$B_1 - H_1 = 4\pi g_1/c, \quad B_2 - H_2 = 4\pi g_2/c,$$

while

$$B_1 = \mu H_1 \quad \text{and} \quad B_2 = \mu H_2,$$

which would mean that $B_1 > B_2$. This, however, would contradict the requirement $\partial B/\partial z = 0$ (curl $B = 0$, since there is no electric field), and so we see that it is impossible to have any total current on the surface. The case of a body with B exactly zero is, however, entirely different, for now both B_1 and B_2 vanish identically and there is no need to have $g_1 = g_2$ in order to satisfy $\partial B/\partial z = 0$. Roughly speaking, we can say that in passing across the superconductor the magnetic field vanishes, and so is able to forget what value it ought to have on reappearing at the other side—it can in particular assume a value corresponding to a net current across the surface. Another simple example is that of a long cylindrical wire, where again it is easily seen that in the absence of an electric field, the requirements div $B = 0$, and curl $B = 0$ inside, can be satisfied only if $B = 0$, when there is a current flowing along the surface of the wire.

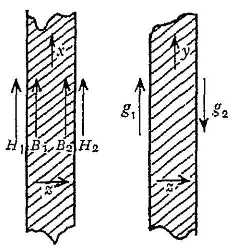

Fig. 5.

Actually, of course, such a total current can never appear in a singly connected superconductor unless it forms part of a circuit containing a source of electromotive force, but as we shall see in Chapter IV, for a multiply connected superconductor (such as a ring), a mere change of the external field is sufficient to induce a total current in the specimen. We may emphasize again that this ability of the surface currents responsible for the magnetism of superconductors to form a total current without any electric field is characteristic only of an *exactly* zero permeability, and sharply distinguishes a superconductor from any

other magnetic body, in which the surface currents producing the magnetism can never lead to any total current.

In as far as these considerations show that there can never be any electric field inside a body with $B=0$, but that a total current can nevertheless flow, we see that the apparent absence of resistance in the superconducting state is really a secondary feature, and does not at all mean that superconductivity is a limiting case of high conductivity. In fact the resistance measurements merely confirm the fact that an electric field cannot exist in a superconductor, and give no information about the conductivity; in a sense the idea of conductivity even loses its physical meaning in the superconducting state, since in the absence of an electric field the conductivity can never be measured. Without the resistance measurements and the confirmation of the occurrence of persistent currents in a superconducting ring, we could not, however, be sure that the small value of B indicated by the magnetic measurements could really be interpreted as an exactly zero value.

The result of these considerations, then, is that a superconductor should be described as a body into which a magnetic field cannot penetrate. We have seen that the description of superconductivity as a limiting case of high conductivity cannot explain the Meissner effect, but the new description which sets out from the Meissner effect, supposing that B is really exactly zero inside a superconductor, can explain the zero resistance of a superconductor, and is therefore fundamental.

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Chapter III

THE INTERMEDIATE STATE

Owing to the relatively large value of the diamagnetic susceptibility of a superconductor, it is evident that its magnetic properties will depend on the shape of the specimen, for any magnetic field that is applied will be distorted by the presence of the specimen. For this reason, except in the simplest case of an infinite cylinder parallel to the applied field, the field will reach the critical value H_c at some places on the surface of the specimen earlier than others, when the applied field is steadily increased. As soon as the field reaches H_c at any place, the metal can no longer remain superconducting there, and superconductivity must begin to disappear; as the external field is farther increased some sort of transition must take place, until when the external field reaches H_c, the transition is completed, and the specimen is entirely in the normally conducting state. In this chapter we shall discuss how this transition takes place in connection with the magnetic properties of superconducting ellipsoids, and also describe briefly the experimental methods which have been used for studying these properties and the results obtained.

If the whole of the specimen is superconducting (i.e. if the applied magnetic field is not too large), the magnetization of the specimen and the field distribution round it can be obtained by applying the usual methods to the case of zero permeability. As is well known, an exact solution can be obtained in the case of an ellipsoid in a uniform field along one of the principal axes, and since moreover a non-ellipsoidal shape can introduce other complications of irreversibility (see Chapter IV), we shall at present limit the discussion to the case of ellipsoids. Consider then an ellipsoid of demagnetizing coefficient $4\pi n$ (relative to one of the principal axes), and let H be the external field (i.e.

the field in the absence of the specimen), which we assume uniform and parallel to the given principal axis; if the magnetization produced by this field is I, we can suppose formally that there is a "magnetizing" field* H_i inside the ellipsoid, and this will be uniform, parallel to the external field and given by

$$H_i = H - 4\pi n I. \tag{1}$$

We have, then, that $B = H_i + 4\pi I$,

or, since $B = 0$, $I = -H/4\pi(1-n)$. (2)

Thus the slope of the magnetization curve of a superconducting ellipsoid is the steeper, the greater its demagnetizing coefficient, i.e. the flatter it is in the field direction. For a long cylinder in the field direction, $n=0$, and (2) reproduces the result already obtained in Chapter II (equation (12)). Other special cases of practical importance are a cylinder with its axis perpendicular to the field, when $n=\frac{1}{2}$, so that $I=-H/2\pi$; a sphere, for which $n=\frac{1}{3}$ and $I=-3H/8\pi$, and a flat disc, with its plane normal to the field, for which $n=1$, and I increases infinitely rapidly (in this case, however, equation (2) is valid over only an infinitely small range of fields, since, as we shall see directly, the field at the edge of the disc immediately exceeds H_c). We may point out that the result (2) could equally well have been obtained from the description of infinite conductivity if the ellipsoid became superconducting in zero field, for as we saw in Chapter II, this case is equivalent to $B=0$; the infinite conductivity description would make a different prediction, however, if the specimen had become superconducting in a non-zero field, while the Meissner

* In Chapter II this field was denoted by H, since for the case considered there of a long cylinder it is identical with the external field; here, however, we use the notation H_i to distinguish between this "magnetizing" field and the external field H. It is important to realize that H_i for a superconductor does not have its usual physical significance of an "internal" field, and is introduced really only as a mathematical device. Thus, as was implied in the discussion at the end of Chapter II, the state inside a superconductor is completely determined by the value of B $(=0)$, independently of the external conditions, while H_i, as can be seen from fig. 4*b*, is not uniquely determined for $B=0$. We shall see below that H_i has the same value as the field outside the equator of the ellipsoid.

effect shows that (2) must be valid independently of the initial conditions.

Let us now consider the actual field H_e outside the ellipsoid; the vector H_e must be entirely tangential at the surface, since the normal component has to be equal to the normal component of B inside (i.e. equal to zero). The magnitude of H_e has to be equal to the tangential component of H_i at the surface in the usual way, so that

$$H_e = (H - 4\pi nI)\sin\theta, \tag{3}$$

where θ is the angle between the normal to the surface and the external field direction (parallel to H_i). As we move away from the ellipsoid the field H_e decreases in magnitude, and becomes more parallel to the vector H, until at great distances the field is no longer distorted by the presence of the specimen, and $H_e = H$.* Evidently the maximum value of H_e at the surface will be on the equator (i.e. where the surface is parallel to the external field H), and this maximum value is

$$H_e = H_i = H - 4\pi nI = H/(1-n). \tag{4}$$

Thus as soon as $H > (1-n)\,H_c$, the field at the equator will exceed H_c, and we might expect parts of the specimen to go over into the normal state with a consequent drop of the diamagnetic magnetization. At first sight it might seem that this transition would take place by a progressively larger region round the equator reverting to the normal state, with some boundary surface separating it from an inner still superconducting region, until when $H = H_c$, the inner region was completely "eaten away", and the whole specimen was in the normal state; this transition mechanism, however, leads immediately to difficulties. Suppose for instance that at some stage of the transition

* The exact field distribution is very easily obtained in the case of a sphere (see for instance Jeans, *Electricity and Magnetism*, 4th edition, p. 228). For a sphere of permeability μ in an originally uniform field H in the x direction, the field at any point is given by grad ϕ, where inside $\phi = 3Hx/\mu + 2$, while outside, at distance r, $\phi = Hx\left\{1 - \frac{\mu - 1}{\mu + 2}\left(\frac{a}{r}\right)^3\right\}$ (a is the radius of the sphere).

there is a boundary surface, as shown in fig. 6, between an inner superconducting region and an outer normal one. Evidently this boundary will be determined by the condition that the field is just equal to H_c on it (or is less than H_c where the boundary coincides with the surface of the specimen); the field, however, outside such a convex* superconducting region will be less than at its surface (just as in the case of an ellipsoid, as already pointed out), and consequently in the region between the boundary surface and the ellipsoid, the field is less than H_c, and there is no reason why this part should be in the normal state. It is in fact impossible to find a simple boundary surface which satisfies simultaneously the conditions that the field should have the value H_c over it, and that the field should be greater than H_c in the region between it and the surface of the ellipsoid. This means that when $H > (1-n) H_c$, the ellipsoid must split up into some arrangement of superconducting and normal regions, more complicated than that suggested in fig. 6, and we shall see later that the division is a very fine one. Peierls (1) and London (2) have shown, however, that the macroscopic magnetic properties of the ellipsoid, when it is split up in this way, i.e. when

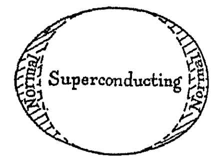

Fig. 6.

$$H > (1-n) H_c,$$

can be obtained without any detailed knowledge of the structure of this fine division, by assuming that on a macroscopic scale the specimen is in a uniform "intermediate state" (the uniformity is justified by experiment), with B intermediate between 0 and H_c, and $H_i = H_c$ (it will be remembered that this is the value of H_i just before commencement, and after termination of the intermediate state). Before considering the actual structure of the metal in this intermediate state, we shall first of all show how this macroscopic theory provides a natural description of the

* It can easily be seen that some part of the boundary will have to be convex.

transition between super and normal conductivity in an ellipsoid.

Assuming, then, that when H_e exceeds H_c, i.e. when

$$H > (1-n)\,H_c$$

the specimen enters the intermediate state as defined above, we have

$$H_i = H_c, \quad \text{or} \quad H - 4\pi n I = H_c,$$

so that

$$I = (H - H_c)/4\pi n. \tag{5}$$

This result is obviously reasonable, for at the two ends of the intermediate range it makes predictions which are evidently correct. Thus for $H=(1-n)\,H_c$ it gives $I=-H_c/4\pi$, which is also given by equation (2) (equation (2) is of course valid, since for this field the whole of the specimen is still superconducting); also for $H=H_c$, equation (5) satisfies the obvious requirement that the specimen should be entirely in the normal state ($I=0$).

The value of B in the intermediate state is also easily obtained, for $B=H_i+4\pi I$, or $B=H+4\pi(1-n)\,I$, so that substituting from equation (5), we find

$$B = H_c - (H_c - H)/n. \tag{6}$$

We see then that as soon as the external field exceeds the value $(1-n)\,H_c$, the induction in the specimen ceases to be zero, and grows linearly from zero to H_c; beyond this point the penetration of the lines of force is complete, and $B=H$. In the intermediate state the magnetizing field H_i ($=H_c$) has already its usual physical meaning, since it is no longer ambiguous for a given value of B; it is, in fact, the field which would be observed in a small canal parallel to the direction of the external field. We may emphasize again (see footnote, p. 22) that this is not true in the purely superconducting state, when $B=0$, for then it can easily be seen that the presence of a canal alters the field distribution in such a way that the field observed in the canal bears no relation to the H_i of equation (1); this is particularly the case if the canal passes right through the specimen, for then the specimen is no longer singly connected, and as in the case

of a ring, the field in the canal always remains constant (see Chapter IV). Even if the canal does not pass right through the body, the end of the canal causes a distortion of the field such as to make it vanish inside the canal. In the case of the intermediate state, however, just as in any ordinary magnetic body, the distortion produced by the ends of the canal can be neglected, and the field in the canal is really H_i.

The field distribution round a sphere in the intermediate state can be deduced from the formula on p. 23 (footnote), if we put for μ the value of B/H_i, and for n the value $1/3$, i.e.

$$\mu=\frac{1}{n}\frac{H}{H_c}-\frac{1-n}{n}=3\frac{H}{H_c}-2. \tag{7}$$

These ideas of an intermediate state were actually introduced to explain results of experiments on the magnetic properties of superconducting specimens in the transition from the superconducting to the normal state, and we shall now describe briefly how these experiments fit in with the theory outlined above. It is convenient to mention here all the experimental methods which have been used for investigating magnetic properties of superconductors, since some of them have been applied to problems which we shall discuss later; there will be no need to describe the methods in any detail, since they are for the greater part merely modifications of well-known magnetic methods.

(1) In the original experiments of Meissner and Ochsenfeld (3), the field at various places round the specimen was measured by means of search coils which could be turned over. This method (also used by Tarr and Wilhelm (4) in experiments which confirmed the Meissner effect) has the disadvantage that it gives only the average field over the area of the search coil, and it involves somewhat complicated devices for setting and rotating the coil, but it is useful in special cases—for instance, if a large specimen can be used.

(2) Mendelssohn and Babbitt (5) measured the field at the equator of a tin sphere by means of a bismuth wire (at low tem-

peratures the resistance of a bismuth wire is strongly field dependent).* Their results confirmed on the whole the behaviour predicted by the above discussion; thus for $H < \frac{2}{3}H_c$, the field at the equator was approximately $\frac{3}{2}H$, while for $H_c > H > \frac{2}{3}H_c$, the field at the equator was approximately constant and equal to H_c. The approximate nature of the confirmation was due to the fact that the bismuth wire was not of negligible thickness, so that the field measured was rather less than that actually at the equator, and also due to slight impurities in the tin, which as we shall see later strongly influence the magnetic properties. A rather more detailed survey of the field round a tin sphere was later made by de Haas and Guinau (7), using the same method, and they also measured the field inside various canals in the sphere. The results are shown schematically in fig. 7*a*, the broken line showing the variation of the field at the equator (which is equal to H_i) and the full line that of the field at a pole (equal to B). It will be seen that the curves agree with the theoretical predictions,† i.e. for $H < \frac{2}{3}H_c$, $H_i = \frac{3}{2}H$, $B = 0$, for $H_c > H > \frac{2}{3}H_c$, $H_i = H_c$, $B = 3H - 2H_c$ and for $H > H_c$, $H_i = B = H$. The field measurement in the canal confirmed very directly that the field H_i is indeed equal to H_c in the intermediate state (i.e. for $H_c > H > \frac{2}{3}H_c$), but, as we have already pointed out, this field cannot give H_i for the superconducting state. In fact for H increasing, the field in the canal was zero until the intermediate state was reached, and for H decreasing it was constant, equal to H_c, right down to zero H; this is exactly what we should expect, since the canal goes right through the sphere and thus makes it similar to a superconducting ring (see Chapter IV).

(3) Rjabinin and Shubnikov (8) measured the total induction of the specimen by removing it suddenly from inside a long coil, and observing the ballistic throw of a galvanometer connected

* This method was first applied to problems of superconductivity by de Haas and Casimir-Jonker (6).

† Actually the curves were not quite reproduced when the field was reduced from below H_c, but these irreversibilities can probably be ascribed to slight impurities in the tin.

in series. They also sometimes used an almost identical method, in which the throw was observed for a sudden change of field, the specimen remaining in the coil. Their experiments were made with long cylinders parallel to the field, and so are not relevant to the intermediate state, but they are of interest as confirming the Meissner effect in its application to the magnetization curve of a long cylinder (i.e. confirming the behaviour described in Chapter II). The same type of method has been used by Mendelssohn and his collaborators in various investigations (see Chapter VI), including some experiments on spheres.

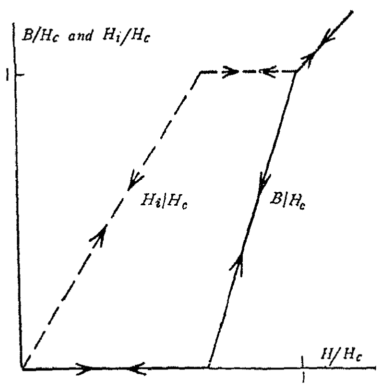

Fig. 7*a*. *B*-*H* curve and H_i-*H* curve for a sphere (schematic representation of results of de Haas and Guinau (7)).

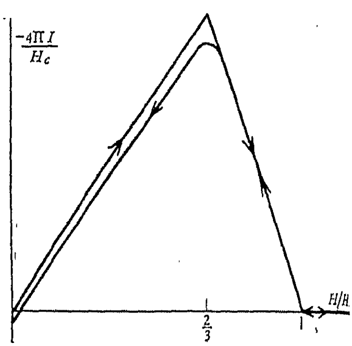

Fig. 7*b*. Magnetization curve of a lead sphere (Shoenberg (9)).

(4) Shoenberg (9) used the direct method of measuring the force on the specimen in a slightly inhomogeneous field. This force divided by the field gradient then gives the magnetization. This is of course nothing else than the well-known Faraday method of determining susceptibilities, and is particularly simple to apply owing to the very strong diamagnetism of superconductors, so that the balance used for measuring the force has not to be particularly sensitive. In fig. 7*b* we reproduce the magnetization curve of a lead sphere obtained with this method. It will be seen that it agrees well with the theory

developed above. Initially, the slope is indeed very close to the calculated value $\frac{3}{8}\pi$, while beyond $\frac{2}{3}H_c$ (when the field should begin to penetrate the sphere) the curve turns sharply downwards and is fairly accurately linear, the magnetization vanishing at and above H_c. On again reducing the field, the curve is retraced practically without hysteresis, thus again confirming the Meissner effect (the slight hysteresis can as usual be explained by departure from ideal conditions and is probably due to slight impurities).

(5) Another method, used by Shoenberg (10) and by Daunt (11) for investigating the nature of the intermediate state, is to measure what is effectively the alternating field susceptibility of the specimen. This can be done by observing with an A.C. method the change of self-inductance of a coil when the specimen is inserted (in Daunt's work, the change of mutual inductance of two coils was observed); the alternating field of the measuring current in the coil was superposed on a steady field which brought the specimen into the required state. The experiments confirmed the zero permeability property of the purely superconducting state, but as soon as the intermediate state set in the results were greatly complicated by the appearance of energy losses, produced in the specimen by the alternating field. It is not possible to describe here the details of the results, since they are connected in a rather complicated way with the theory, and moreover the detailed interpretation of many features is as yet far from clear, but the general conclusion of the work was, that the metal has a non-zero resistance in the intermediate state (i.e. the energy losses are due to eddy currents), and that this resistance is different in different directions in the specimen. The appearance of eddy currents confused the magnetic properties, but in a special experiment with a sphere made up of thin laminations the effect of the eddy currents was greatly reduced, and the specimen did indeed behave as if the magnetic properties in the intermediate state were given by (5) above (in the absence of eddy currents the experiment gives

effectively dI/dH, and for the laminated sphere this did indeed change sign and roughly double its magnitude, in a narrow range of fields near $\frac{2}{3}H_c$). We shall return to some other features of these experiments later.

In connection with this summary of experimental methods, we may mention that all of these magnetic methods, but particularly (3), (4) and (5), are often much more convenient than the electrical method (i.e. measurement of resistance), for testing for superconductivity, for determining critical fields, and for examining how far a specimen behaves like an ideal superconductor (in the sense explained in Chapter 1). An obvious advantage of the magnetic methods is that no leads have to be attached to the specimen, and for some purposes, moreover, the shape of the specimen may be left quite arbitrary, so that the material to be tested can be used in the form in which it is available, without any mechanical treatment. Another advantage is that the magnetic methods generally give the volume properties of the specimen, while the electrical method gives effectively the resistance only of the path of least resistance; thus we shall see later that superconducting alloys may have zero resistance in very high magnetic fields, while the magnetic methods show that actually only a very small fraction of the volume is still superconducting. The use of a magnetic method (actually one of type (3)) to search for new superconductors was first applied by Kürti and Simon (12) in the range of very low temperatures opened up by the paramagnetic salt demagnetization technique and three new superconductors were found in this way.

So far we have described the intermediate state merely by its macroscopic magnetic properties, but have left open the question as to whether the structure corresponds to some complicated mixture of the purely superconducting and normal states as suggested on p. 24, or whether it really represents a new third state of the metal. The former possibility is suggested from the experimental point of view by the electrical properties of the

metal in the intermediate state—we have already mentioned the evidence of alternating field experiments that the metal has non-zero resistance in the intermediate state, but even more direct evidence is furnished by resistance measurements on long cylinders in transverse magnetic fields (13). In fig. 8 we reproduce some experimental curves, showing how the resistance of such a cylinder varies with the strength of the transverse field,* and it will be seen that the resistance begins to return at

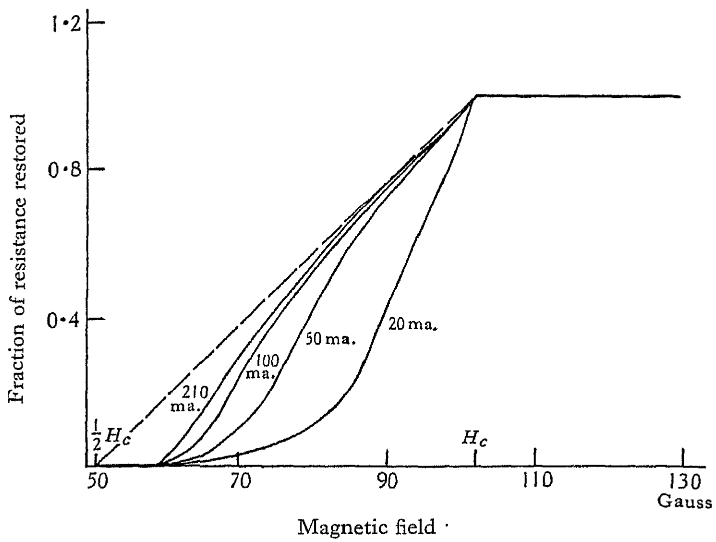

Fig. 8. Restoration of resistance of monocrystalline tin wire by a transverse magnetic field. Diameter of wire 0·25 mm. $T=2{\cdot}92^\circ$ K. (de Haas, Voogd and Jonker (13).)

approximately half the critical field, i.e. as soon as the cylinder enters the intermediate state. That this return of resistance at $\frac{1}{2}H_c$ is really connected with the commencement of penetration was shown by an experiment with a cylinder of elliptical instead of circular cross-section, when, corresponding to the different demagnetizing coefficient, the resistance began to return at a

* The influence of the measuring current, shown in fig. 8, will be discussed later.

different field value. It is interesting to mention that when von Laue (14) first suggested that the return of resistance at $\frac{1}{2}H_c$ in the case of a circular cylinder in a transverse field was connected with the field being twice as great at the "equator" of the cylinder cross-section as it would be in a longitudinal field, the idea of an intermediate state had not been introduced, and it remained a mystery why resistance should reappear if superconductivity was destroyed only at the very equator (for it seemed that a superconducting path would still be left open through the core of the cylinder).

This evidence for a resistance in the intermediate state which grows with increase of the external field (i.e. with increasing field penetration) does indeed fit in with the hypothesis that in the intermediate state the metal is divided up into microscopic superconducting and normal regions, arranged in such a way that a current has to pass partly through the normal regions. Since at a boundary between a superconducting and a normal region the magnetic field in the normal region has to be entirely tangential to the boundary, it can easily be seen that the field must penetrate into the specimen either through long sausage-shaped or else razor-blade normal regions, and the presence of resistance perpendicular to the external field indicates the latter type of regions. We may mention in this connection an interesting experiment of Shubnikov and Nakhutin (15), who showed that a sphere in the intermediate state has a resistance perpendicular, but not parallel, to the direction of the external field, thus confirming rather directly that the sphere is indeed divided up into alternating superconducting and normal laminae. Less direct evidence for this type of structure was provided by the alternating field experiments with a sphere, which also suggested that the resistance of the sphere in the intermediate state was anisotropic.

Since there is no induction in the superconducting regions and the induction in the normal regions is H_c, while the average induction is the value of B observed for the whole specimen, it

is evident that the fraction x of the specimen in the normal state is given by

$$x = B/H_c; \tag{8}$$

in order, however, to be able to say anything about the absolute thicknesses of the individual laminae, we must consider in greater detail the structure of the intermediate state. Landau (16) has investigated the question theoretically by a method analogous to that used in determining the domain structure of ferromagnetics, and shown that for a specimen with a non-zero value of B the energetically most favourable distribution is indeed one with a large number of alternatively superconducting and normal laminae. The number of laminae (and hence their thicknesses) has to vary from the inside of the specimen towards the surface, for in order to avoid the difficulty (analogous to that discussed on p. 24) of having a field less than H_c in the normal laminae just outside the convex ends of the superconducting laminae,* it is necessary to have the laminae at the boundary of the specimen thinner than the depth of penetration of a magnetic field into a superconductor, so that the ordinary macroscopic description, $B=0$, no longer applies for the superconducting laminae close to the surface of the specimen. By means of a kind of branching process, the laminae become thicker, and consequently fewer in number, towards the inside of the specimen, as shown in fig. 9 for the case of a flat plate in a transverse magnetic field. The absolute values of the greatest thicknesses z_s and z_n of the laminae (i.e. at the centre of the specimen) are determined by the coefficient of surface tension α between the superconducting and normal phases and the length d of the specimen in the direction of the magnetic field; z_s and z_n are given by the equations

$$z_n z_s^2 = \frac{32\pi\alpha}{H_c^2}(\sqrt{2}-1)^2 d^2, \quad \frac{z_n}{z_s} = \frac{B}{H_c - B}, \tag{9}$$

where B is the induction in the specimen (given by equation (6)).

* This difficulty was overlooked in an earlier version of Landau's theory (17).

If we write this, for the special case $B=\frac{1}{2}H_c$, as

$$z_n=d_0^{\frac{1}{3}}d^{\frac{2}{3}}, \tag{10}$$

where

$$d_0=\frac{32\pi\alpha}{H_c^2}(\sqrt{2}-1)^2,$$

we see that the layer thickness is small compared with the specimen size only provided the specimen size is large compared with d_0; since d_0 has the dimensions of a length, it is natural to

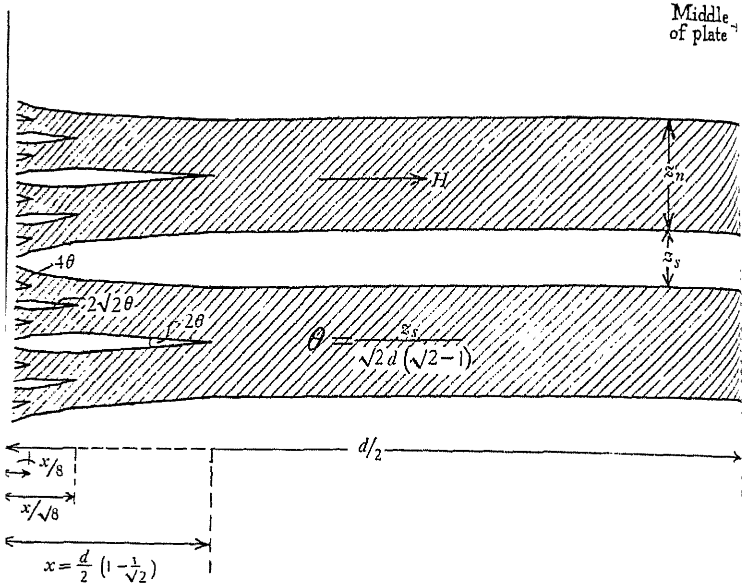

Fig. 9. Penetration of a magnetic field into a plate in the intermediate state (Landau (16)).

suppose that it is of the order of magnitude of the depth of penetration of a magnetic field into a superconductor. In fact, if the specimen is small enough to be comparable to the penetration depth, the whole idea of an intermediate state loses its meaning, and we can say nothing about how the superconducting transition in a magnetic field will take place, until we understand the behaviour of superconductors of small dimensions.

We shall see in Chapter VII that the position is at present obscure both from the experimental and the theoretical point of view, but the present evidence indicates that the penetration depth is of order of magnitude 10^{-5} cm., so that we can guess from equation (10) that the laminar thickness in a plate 1 cm. across is of order of magnitude $2 \cdot 10^{-2}$ cm.; it is, however, very difficult to devise a way of measuring this thickness, since at the surface of the plate the thickness becomes much smaller by the branching process described above, and the specimen should appear to be quite uniform from outside.

Landau's theory is important in showing that the intermediate state is not really a new state, but merely a special kind of mixture of the familiar superconducting and normal phases; it cannot, however, explain certain other features of the intermediate state which we shall describe below, some of which are probably connected with the properties of the very thin laminae which the theory shows must occur at the surface of the specimen. Thus, when the thickness of the laminae becomes comparable to d_0, as at the surface of the specimen, it is no longer possible to speak of separate superconducting and normal phases, and we have a kind of mixed phase, about whose properties very little can be said in the absence of a more complete theory which can explain the properties of superconductors of small dimensions. We now come to the features of the intermediate state for which there is as yet little more than speculative explanation.

(1) The most important of these features is that the resistance of the metal in the intermediate state depends on the strength of the measuring current much more than could be expected from the effect of the magnetic field of this current at the surface of the specimen. Since the current must flow normally to the laminae, and the fraction of the metal in the normal state is B/H_c (see equation (8)), we should expect that the resistance should also vary as B/H_c, i.e. linearly from zero to its full normal value, independently of the weak measuring current

(see the broken line in fig. 8). Actually, however, as can be seen from fig. 8, the resistance of a cylinder in a transverse magnetic field is smaller, the smaller the measuring current, even when the field of the latter is as small as $4 \cdot 10^{-3} H_c$, and the resistance is in general less than would be given by the linear relation. Similarly, in the alternating field experiments described on p. 29, the average resistance of the sphere was found to decrease markedly with the amplitude of the alternating field (i.e. with the strength of the eddy currents in the sphere), down to amplitudes as low as $3 \cdot 10^{-5} H_c$. Over a considerable range of current strengths, the resistance for a given external field decreases very roughly as the logarithm of the current, so that very sensitive methods are required if we wish to extrapolate the resistance down to vanishingly small currents. The methods used up to now have not allowed of an extrapolation to sufficiently low currents, but both the alternating field experiments and some recent experiments of Misener (18) on wires in a transverse field (using a very sensitive potentiometer method), suggest that possibly the resistance might actually vanish with zero measuring current; this suggestion should, however, be regarded as speculative until further experimental evidence is available.

It seems that the only way of reconciling these electrical properties of the intermediate state with the laminar picture is to attribute the anomalous behaviour to the mixed phase which, as we mentioned above, must occur at the surface of the specimen. We must suppose, in fact, that for very low currents the mixed phase has a resistance much lower than that offered by the laminae in the interior of the specimen—perhaps even vanishing for the limiting case of zero current—and that this resistance increases with the strength of the current. We should then suppose that, for very low currents, the resistance of the specimen was determined mainly by the properties of the mixed phase at the surface of the specimen, while for stronger currents the resistance would be mainly determined by the properties of the laminar structure in the interior of the specimen. Thus for

increase of current we should expect on this hypothesis that the resistance-field relation should approach linearity, and this seems to be in rough agreement with the observed facts. In order to investigate this hypothesis further it would be necessary to study the effect of varying the diameter of the wire, but there are at present very few data available in this respect.

(2) Misener (18) has measured the resistance of separate short sections ($\sim$1 mm. long) of a long wire in a transverse magnetic field, and found that for any given field in the intermediate range (i.e. $H_c > H > \frac{1}{2}H_c$), the fraction of the normal resistance restored varied considerably from section to section, some being nearly superconducting while others had nearly their full resistance. At first sight this seems to conflict with the theory, according to which the wire should appear uniform from the outside, and if the experiment is interpreted as indicating laminae of thickness of order 1 mm., it conflicts with the usual estimates of the penetration depth (Chapter VII). We think, however, that it would be premature to reject the laminar theory on the basis of this experiment, since an equally probable explanation is that the results are due to non-uniformity of the specimen. We have seen in (1) above that the surface conditions probably play an important role in determining the resistance in a transverse field, owing to the occurrence of the mixed state, and from the experimental conditions we could indeed expect a non-uniform surface (e.g. owing to the clamping of the potential leads to the specimen). Further experiments on this effect (for instance at high measuring currents) would evidently be desirable.

(3) Although the magnetic experiments in the case of a long cylinder in a transverse field confirm that the field does indeed begin to penetrate at $\frac{1}{2}H_c$, the resistance of the cylinder in some cases does not begin to return until a slightly higher field value. Thus in the Leiden experiments, the return of resistance often commenced at $0{\cdot}58H_c$ (this feature can be seen in fig. 8, but to avoid confusion we refrained from pointing it out earlier). Recent experiments of Burton and Mann (19), and Misener (18),

have shown, however, that the figure 0·58 is obtained only if the temperature is relatively far below the normal transition temperature, and that the theoretical value $\frac{1}{2}$ is approached close to the normal transition temperature (i.e. for low critical fields).*

The temperature dependence of this feature, and the fact that it occurs in very pure specimens, suggests that the non-appearance of resistance at exactly $\frac{1}{2}H_c$ (i.e. at the moment when penetration commences) may be due to some effect analogous to supercooling, but it is also possible that the state with zero resistance for the field between 0·5 and 0·58 H_c is a stable one and is caused by some property of the mixed phase at the boundary of the specimen, or is due to the small thickness of the normal layers in the initial stages of the transition. We may point out that most of the experiments have been made with rather thin wires (radius $\sim 10^{-2}$ cm.), so that the thickness of the normal laminae in the intermediate state will be very small, especially in the initial stages of the field penetration. Perhaps the 0·58 anomaly may be connected with anomalous properties of such thin laminae—the temperature dependence being due to the temperature dependence of the d_0 of equation (10) (i.e. the variation of laminar thickness with temperature). In this connection systematic experiments on wires of different diameters would be of interest.

(4) Perhaps connected with the last feature is the phenomenon of a time lag in the penetration of the magnetic field into the specimen in the intermediate state. de Haas, Engelkes and Guinau (20) have shown in fact, that after a sudden change of the external field, the field distribution of a sphere in the intermediate state assumes its final form only gradually. The time lag is of order 15 mins. near the commencement of the intermediate state, i.e. at $\frac{2}{3}H_c$, and decreases with increasing penetration of the external field, until it is negligible when penetration is

* This can also be seen from some of the Leiden data; see for instance (13). Misener finds that if the ratio of the transverse field at which the resistance first appears to H_c is plotted against temperature, a straight line is obtained, the slope of which is approximately the same for tin, lead and indium.

complete. No such time lags were, however, observed in the experiments of Shoenberg, in which the magnetic moment of the sphere was measured; this may be connected with the fact that the sphere was several times smaller than that used in Leiden, but we are more inclined to the view that the time effects observed were due to secondary causes. This is suggested by the fact that more marked time lags have been found by Mendelssohn and Pontius (21) for specimens of non-ellipsoidal shape (where the transition is more complicated than for an ellipsoid—see Chapter IV), and so it is possible that the effects observed for a sphere are due to irregularities of shape, such, for instance, as the holes bored through the sphere for internal field measurements.

(5) In certain cases, when the magnetic field is reduced below H_c, the specimen appears to remain in the normal state until the field is 2 or 3 per cent below H_c, when suddenly the magnetic properties assume the form they should have for the intermediate state (21) (this can be seen for instance in fig. 11, p. 50). What is probably an allied effect is observed also in resistance measurements on a long cylinder in a longitudinal field, where the resistance suddenly disappears at a field slightly lower than the field at which the resistance appeared for increase of field (13).* These effects are observed only in very pure specimens, but are never quantitatively very reproducible, and so are probably analogous to supercooling in ordinary phase transitions. H. London (22) has pointed out that such a supercooling may be related to the surface tension between the superconducting and normal phases, but the detailed connection has not been worked out.

We have now touched on most of the phenomena connected with the transition of ellipsoids between superconductivity and normal conductivity caused by magnetic fields, and although

* This particular effect was found, however, to depend very much on the method of connecting the potential leads to the specimens (being much greater for soldered than for welded leads), so it may be partly of secondary origin due to some effect of the solder alloy at the junctions.

the general nature of the transition is fairly clear, we have seen that there are many detailed features still requiring explanation. It is not, however, yet definite which of these are fundamental and which are due to "non-ideal" conditions. We shall see in Chapter IV that the intermediate state can also explain the transition caused by a current alone, and in Chapter V we shall deal with the thermodynamics of the intermediate state.

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Chapter IV

THE SUPERCONDUCTING RING AND DISTURBANCE OF SUPERCONDUCTIVITY BY A CURRENT

A multiply connected body, such as a ring, differs essentially from a singly connected one in that it is possible to induce a "total" current round it, in the sense that closed circuits can be drawn enclosing parts of the body (but nowhere passing through it) which enclose a net flow of current. If the body concerned is not superconducting, any such total current is always associated with an electric field, so that Joule heat is produced and the current cannot maintain itself; in a superconductor, however, the current, as we have seen, is of the same nature as the surface currents responsible for ordinary magnetism, and is not associated with any electric field, so that it can flow indefinitely.

To illustrate the peculiar magnetic properties caused by the possibility of inducing such "persistent" total currents, we shall consider a case which can be treated mathematically, that of a circular ring* of mean radius R, made of a wire of circular cross-section and radius r, small compared with R. If the self-inductance of the ring is L, then any change of a magnetic field H normal to the plane of the ring will cause a change of the total current i round the ring, given by

$$L\, di/dt - \pi R^2\, dH/dt = 0,$$

which expresses the fact that there is no electromotive force in the superconducting ring. Integrating this, we find

$$Li = \pi R^2 (H - H_0), \qquad (1)$$

where H_0 is the value the field had when there was no current in

* The results which do not involve the circular symmetry of the ring apply of course to any type of ring; other results are, however, only qualitatively applicable to non-circular rings.

the ring. If there were no current flowing, the ring would have just the magnetic moment of a long wire in a transverse field (to a first approximation the fact that the wire is bent into a circle is irrelevant), i.e. $-\pi Rr^2H$ would be the moment in field H. The total current i, however, gives the ring an additional magnetic moment $-\pi R^2 i$, which is of the order of magnitude $(R/r)^2$ times larger (this can be seen by substituting the value of L from equation (3) below, but it is qualitatively evident, since the moment due to the total current is of the order of magnitude of the moment of a sphere of radius R, while the moment of the ring when there is no current is proportional only to the volume of the superconducting material in the ring). Actually, of course, this division of the magnetic moment into two parts is somewhat artificial, but it is a convenient way of describing the real current distribution, which consists of a surface current unevenly spread over the cross-section of the wire. The current i represents the mean current flowing in one direction, while the currents responsible for the magnetic moment when $i=0$ are those which remain when i has been subtracted: roughly speaking these are equal currents in opposite directions, flowing along the inside and outside surfaces of the ring. It is because these equal and opposite currents flow so close to each other, that their magnetic moment is so small relative to that of the net current i in one direction.

We see at once from equation (1) that the magnetic properties of a ring differ essentially from those of a singly connected body, for the value of the magnetic moment depends entirely on the initial conditions. If, for instance, the ring was cooled below its threshold temperature in zero field, $H_0=0$, and the current is given by

$$Li=\pi R^2 H, \tag{2}$$

while if it was cooled in field H_0, the current is given by equation (1), and in particular when the field is reduced to zero after the cooling, a current $-\pi R^2 H_0/L$, corresponding to a large "paramagnetic" moment, is left flowing in the ring. This lack

of uniqueness of the magnetic moment is very similar to that which we deduced for a metal of infinite conductivity, and arises from the fact that the current round the ring is induced in such a way as to keep the flux through the hollow of the ring constant. Now in the hollow of the ring (or inside a metal of infinite conductivity such as discussed in Chapter II) $B=H$, so that the current induced will depend on the initial value of H; for a singly connected superconductor the surface current is also induced in such a way as to keep the flux across any cross-section constant, but here the constant value is always zero independently of the value of the external field in which the body became superconducting, because, as we have seen, a superconductor has zero permeability. In other words, the difference between a singly connected superconductor and a superconducting ring, or any merely infinitely conducting body, is that in the former the permeability is zero all over any cross-section, whatever flux passed through it originally being always completely pushed out when it becomes superconducting, while in the latter the permeability of most (or all) of the cross-section (e.g. the hollow, in the case of the ring) remains unity, so that a field H_0 can remain in the hollow of the ring even when it has become superconducting; or, in the case of the infinitely conducting metal, inside the metal after it has become infinitely conducting.

The constancy of the current in a superconducting ring offers the most accurate confirmation of the effectively zero resistance of the metal in the superconducting state. If in fact there was any electromotive force associated with the current, energy would be lost in the form of Joule heat, and the current would die away in accordance with the relation

$$L\,di/dt+wi=0,$$

if w was the resistance of the ring (i.e. the ratio of the e.m.f. to the current), or $$i=i_0e^{-wt/L}.$$

The time of decay of the current, $\tau=L/w$, for a metal at low

temperature but not superconducting is, for any practical dimensions of the ring, extremely small, usually a small fraction of a second; for a superconductor, however, even with a ring of very thin wire or a thin film coated on a non-superconducting wire (to increase the value of the hypothetical w), no decay of the current could be observed over several hours, and in this way, from the limit of change of current which the experimental method used could detect, an upper limit to any possible value of w could be deduced (see p. 3).

Returning to the discussion of the magnetic properties of a superconducting ring, we shall now describe the experimental results. Shoenberg (1) has investigated the magnetic properties by measuring the total magnetic moment of the ring with the force method (we may mention that this method has the disadvantage that only rather small rings can be used, and consequently it is very difficult to make the ring sufficiently uniform in cross-section for an exact comparison with the theory), while Grayson Smith and Wilhelm (2) and Shubnikov and Chotkevitch (3) measured the field at various places round the ring, and thus deduced the magnetic properties. In fig. 10 we show how the magnetic moment of a ring which was cooled in zero magnetic field varies with subsequent increases and decreases of a field normal to the plane of the ring (actually this diagram is a slightly idealized version of the experimental results, which in some details are confused by other factors which are of no interest here). Initially the magnetic moment increases with the field just as explained above; when the moment of the ring, in the absence of a total current, has been subtracted, the slope of the line OA agrees very well with equation (2), and it is interesting to mention that this agreement confirms the fact that the current flows only over the surface of the ring (the absence of any current in the body of a superconductor is of course implied by $B=0$). Thus the experiments show that equation (2) is verified quantitatively only if for L we put

$$L=4\pi R(\log_e 8R/r-2), \qquad (3)$$

the value it assumes for an entirely superficial current, and which differs by about 10 per cent, for the actual rings used, from the value

$$L = 4\pi R(\log_e 8R/r - \tfrac{7}{4})$$

of the self-inductance for a current flowing through the whole cross-section of the ring.*

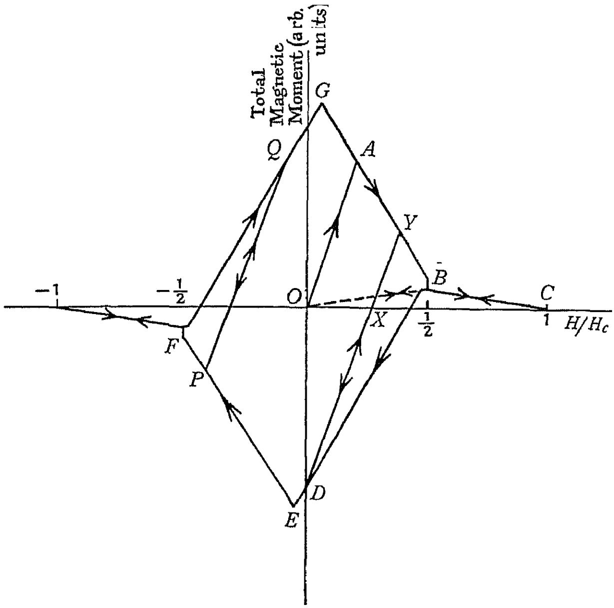

Fig. 10. Magnetization curve of a superconducting ring (schematic).

We see that as soon as the point A is reached, equation (2) ceases to be valid, and the current begins to fall off linearly with further increase of field. The reason for this falling off is that

* The difference between these two values of L was particularly clearly shown by A.C. measurements (1a), but from these it cannot of course be deduced that the current would be superficial for zero frequency—the superficiality of an A.C. current merely points to a very complete skin effect, and shows therefore that the specific resistance of the metal in the superconducting state is small compared with that in the normal state. The upper limit which can be set to this specific resistance by this method is, however, not nearly as low as that obtained by the method explained on p. 43, since the skin effect is already appreciable for the normal state in the conditions used.

the total field at some part of the surface of the ring (in this case, the outer rim) reaches the value H_c when the external field exceeds a certain value which we shall calculate directly. As soon as this happens, resistance reappears in the ring and the current round the ring dies away to a value which will keep the maximum field at the surface just critical, so that the ring becomes superconducting once more. Thus in the section AB of the magnetization curve, the current in the ring decreases with increasing field in such a way as to prevent the field anywhere at the surface of the ring exceeding H_c; the ring is, however, completely superconducting throughout the section OAB, as is shown by the fact that a decrease of field from any point Y on AB causes a change of current in agreement with equation (1) with the superficial value of L, i.e. along a line parallel to OA. An A.C. measurement of the inductance (1a) also showed that the ring was completely superconducting in the region AB as well as OA.*

It is easily seen that the field at the surface of the ring has a maximum value at the *outer* rim of the ring in the section ABC of the magnetization curve, for there, the field H_I of the total current, and the field H_e, which would be there in the absence of a total current, are in the same direction. If we neglect correction terms of order r/R, we have $H_I = 2i/r$ and $H_e = 2H$ (at the outer rim),† so that the field corresponding to the point A is given by

$$2H + 2i/r = H_c, \tag{4}$$

or substituting equation (2) for i, we have

$$H = \left(\frac{Lr}{2\pi R^2}\right) H_c \bigg/ \left(1 + \frac{Lr}{\pi R^2}\right) \tag{5}$$

for the field at which the current begins to fall off.

Beyond A, as we have already pointed out, the current can no

* We may mention here that the interpretation of the region AB of the magnetization curve originally given by the author (1) is definitely erroneous.

† A better approximation has been given by Shubnikov and Chotkevitch (3), but we do not require this for our qualitative considerations. We shall not, however, neglect terms such as $Lr/\pi R^2$, since although proportional to r/R, the proportionality factor is large compared with unity and increases with decrease of r.

longer assume its "full" value $\pi R^2 H/L$, but adjusts itself to satisfy equation (4), or in other words, the current along the section BC of the magnetization curve is given approximately by

$$i = r(\tfrac{1}{2}H_c - H). \tag{6}$$

We see, then, that as soon as the external field H reaches the value $\frac{1}{2}H_c$, there will no longer be any current flowing round the ring (the better approximation shows that at $\frac{1}{2}H_c$ there is still a small current, which disappears discontinuously for further increase of field), and the ring at the same time enters the intermediate state. For further increase of field, the ring behaves exactly in the same way as a long wire in a transverse field greater than $\frac{1}{2}H_c$ (see Chapter III), since there can no longer be any total current round the ring (any total current however small would make the field at the surface of the ring exceed H_c, and moreover, owing to the resistance of the metal in the intermediate state, any such current would in any case die away). In fact, in this region the multiple connection of the ring is no longer of any importance. This was confirmed experimentally by repeating the measurements after the ring had been cut; the experiment showed that the same magnetization was obtained over the range BC whether the ring was cut or not, although of course the magnetization in the range OAB was greatly reduced by cutting the ring (OB refers to the cut ring).

As soon as the external field reaches H_c, superconductivity is completely destroyed and no magnetic moment is left; if now the field is again reduced, the portion BC in fig. 10 is retraced, no total current being induced in the ring. At $H = \frac{1}{2}H_c$, however, the ring becomes completely superconducting again, and further decrease of field induces a current in the ring in a sense *opposite* to that of the current originally induced by an increase of field. Actually the better approximation shows that this happens at a field slightly less than $\frac{1}{2}H_c$, in fact at

$$H = \tfrac{1}{2}H_c/(1 + r/4R).$$

We should thus expect that below $\frac{1}{2}H_c$ the current would be

given by equation (1) with $H_0 = \frac{1}{2}H_c$, since the ring had zero current for this field strength. This current, induced on reducing the field, can, however, never attain its full value, as given by equation (1), for if it were to do so the field would exceed H_c at the surface of the ring. The field at the surface of the ring is now greatest at the *inside* rim of the ring (since the current has now the opposite sense), and the total field there is of magnitude $2H - 2i/r$; thus if i were to attain its full value $(\pi R^2/L)\,(H - \frac{1}{2}H_c)$, this total field would be $(\pi R^2/Lr)\,H_c - 2H(\pi R^2/Lr - 1)$, which is in fact always greater than H_c if, as here, $H < \frac{1}{2}H_c$ (it is easy to show that the dimensionless ratio $\pi R^2/Lr$ is always greater than unity). Since the current cannot attain its full value, it will, as along AB, be given by the condition that the total field at the surface of the ring (this time at the inner rim) is just H_c; in other words the current along the portion BD of fig. 10 will be given by

$$i = -r(\tfrac{1}{2}H_c - H).$$

It should be noticed that the slopes of AB and BD are just equal but of opposite sign (this again is true only to our approximation, and if the magnetization not due to the total current is neglected). Exactly similar considerations show that the portion EF is determined by the condition that the field should be just critical on the outer rim, FG by the condition that it should be critical on the inner rim, and for GAB again on the outer rim. We see that the greatest "persistent" current that can be left in the ring in zero field is given by $2i/r = H_c$, and can be made to flow in either sense round the ring. It may at first sight seem puzzling why the linear portion BD continues to E, for it would seem that as soon as the field was reversed, the greatest magnitude should occur at the outer rim again, where H_I and H_e have the same direction; actually, however, the better approximation shows that the magnitudes of H_I at the inner and outer rims differ by a small quantity proportional to r/R (and similarly for H_e), so that the field continues to be maximum at the inner rim for a little way after the field has been reversed (in fact until E).

Similar considerations explain the position of the turning-point G.

The line $ABDEFG$* can be considered as a kind of boundary curve limiting the possible values that the total current in the ring can assume—anywhere inside this boundary the current varies with a change of field according to equation (1), e.g. along lines such as DX or PQ, parallel to OA, but as soon as the current reaches a point on the boundary curve, any further change of field in the same direction alters the current along the boundary curve itself. This consideration is of some practical interest, for it shows that to produce the maximum "persistent" current in a ring in zero field, it is necessary to cool the ring only in the field corresponding to the point X in fig. 10, and then to remove this field: if the ring had been cooled in zero field, it would be necessary to put on and remove a field at least as large as that corresponding to Y.

We may at this point mention that the magnetization of a singly connected superconductor may also show hysteresis phenomena if it is of complicated shape, and, as we shall explain directly, it is possible that this hysteresis may be due to the "freezing-in" of lines of force in superconducting rings. In some experiments with sharp-rimmed short cylinders (4), the magnetization curve of fig. 11 *a* was obtained when the field was parallel to the axis of the cylinder. First of all, it will be noticed that for increasing fields the curve no longer turns over sharply as in the case of an ellipsoid; this can be interpreted as due to the inhomogeneous distribution of H_i in the cylinder, so that at the sharp rims, for instance, the field reaches the value H_c earlier than in the rest of the specimen. Thus during the transition from

* We give for completeness the equations for this boundary curve obtained with the better approximation of Shubnikov and Chotkevitch (3). These are $i = \mp r\{\frac{1}{2}H_c - H(1 \mp \alpha)\}/(1 \pm \beta)$, where $\alpha = r/4R$ and $\beta = 2\alpha(1 + \log_e 2/\alpha)$; the lower signs are to be taken when the field is critical at the outer rim, and the upper signs when the field is critical at the inner rim (H_c must be taken negative for the sections in the left-hand part of the diagram). The observed magnetic moment will of course also contain a term due to the magnetic properties of the ring with no total current (p. 42).

super to normal conductivity, the specimen probably contains a complicated mixture of superconducting, intermediate, and normal regions (it should be remembered, of course, that the intermediate state is itself a particular kind of mixture of the superconducting and normal phases). On again reducing the external field below H_c, it will be seen that there is a hysteresis* somewhat resembling that found in the magnetization curve of a ring (fig. 10), and a possible explanation might be that owing to the inhomogeneous field distribution, a ring on the surface of

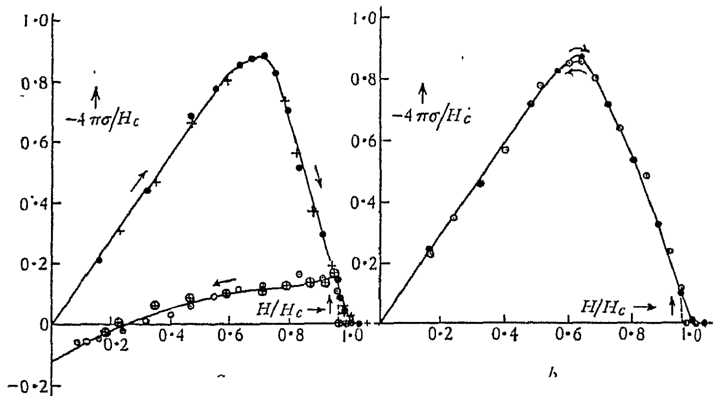

Fig. 11. Magnetization curves of short tin cylinder; σ is the average magnetization (Shoenberg (4)).

a. Field parallel to cylinder axis.
● Increasing field, ⊙ Decreasing field: $T=2{\cdot}04°$ K., $H_c=193$ gauss.
+ Increasing field, ⊕ Decreasing field: $T=2{\cdot}70°$ K., $H_c=129$ gauss.

b. Field perpendicular to cylinder axis.
● Increasing field, ⊙ Decreasing field: $T=2{\cdot}08°$ K., $H_c=191$ gauss.

the specimen was able to become superconducting earlier than the rest of the specimen, when the field was being reduced. For further reduction of the external field a current would be

* As can be seen from fig. 11 *a* the form of the hysteresis was found to be independent of temperature (i.e. the magnetization curves at different temperatures could be made to coincide by a mere change of scale). This temperature independence provides a practical means of distinguishing this sort of hysteresis due to shape from that due to impurities, which is temperature dependent (see Chapter VI).

induced in this ring, thus keeping the flux constant in the interior regions and preventing them from becoming superconducting again.

We should emphasize that the formation of such superconducting rings in a singly connected specimen has not yet been shown theoretically possible, but our qualitative explanation is to some extent supported by two other experimental facts:

(1) It was found that the hysteresis of fig. 11*a* could be considerably reduced by rounding off the rims of the cylinder, which probably made the field distribution more homogeneous, and in terms of our explanation thus delayed the formation of a superconducting ring.

(2) There was practically no hysteresis at all if the field was perpendicular, instead of parallel, to the axis of the cylinder (fig. 11*b*); in this case there is no symmetry round the field direction, and so it is impossible for the specimen to become superconducting all round a section normal to the field simultaneously.

We have already pointed out that when the magnetic field of the current at the surface of the superconductor exceeds H_c the resistance reappears; in the case of a ring, the current then merely adjusts itself to keep the field just critical, and the resistance again disappears, but if the current is maintained constant (by an external source of e.m.f.) the resistance remains. We shall now discuss the changes that take place when superconductivity is destroyed by a current in this way, and for simplicity we shall consider a long cylindrical wire (radius a) with a current i flowing along it.

As soon as the current exceeds the value $\frac{1}{2}aH_c$, the field at the surface becomes greater than H_c and evidently superconductivity will begin to disappear. If we suppose, as at first sight seems plausible, that the transition to the normal state takes place by superconductivity retreating to an inner core of the wire, we get immediately into difficulties rather similar to those discussed in Chapter III in connection with the transition of an ellipsoid

from super to normal conductivity under the influence of an external magnetic field. In fact, if superconductivity were to retreat to a core of radius smaller than that of the wire, all the current would move into this superconducting core, and consequently produce a field even greater than that originally at the surface of the wire, at the boundary of the core with the normal region surrounding it. The retreat of superconductivity would in fact have to continue until the whole wire was in the normal state; this, however, is obviously impossible, since then the current would be uniformly distributed over the cross-section of the wire, and the field would be less than H_c over the greater part of the cross-section (up to a radius $\frac{1}{2}a^2H_c/i$), so that this part could not be in the normal state. This paradox appears even more strikingly if we consider what happens when a wire carrying a current i is cooled below the transition temperature; since in the normal state the magnetic field of the current is zero on the axis and increases as we move away from the axis, superconductivity should appear first of all on the axis of the wire. If it were to do so, however, all the current would immediately move into the newly created superconducting core, and produce a very large field at the boundary of the core, thus destroying its superconductivity once again.

Just as in the case of an ellipsoid in an external field, the paradox shows that the transition must take place in a more complicated manner. F. London (5) and also Landau (6) have shown that since the core cannot be either superconducting or normal, it must be in the intermediate state, with $H=H_c$. It is easy to see then how the resistance will return as the current i is increased. Suppose that $i>\frac{1}{2}aH_c$, and let x be the total current inside a cylindrical surface of radius r. Everywhere inside the core the field has to be H_c, so that

$$2x/r=H_c, \tag{7}$$

and in particular, if r_0 is the radius of the core, and x_0 the current carried by it, then

$$2x_0/r_0=H_c. \tag{8}$$

The current density j is given by $\frac{1}{2\pi r}\frac{dx}{dr}$, which from (7) becomes

$$j = H_c/4\pi r = x/2\pi r^2, \tag{9}$$

so that at the boundary of the core $j_0 = x_0/2\pi r_0^2$. Now at the boundary between a normal and an intermediate region the two states pass smoothly into one another, and so the current density must be continuous across the boundary. In the normal region outside the core, the current density is constant and equal to $(i-x_0)/\pi(a^2-r_0^2)$, so that, equating this to j_0, we find

$$2r_0^2\left(\frac{i}{x_0}-1\right)\bigg/(a^2-r_0^2) = 1. \tag{10}$$

Putting $r_0/a = \rho$, and $2i/aH_c = \lambda$ (λ is then the ratio of the field at the surface of the wire to the critical field, so that $\lambda > 1$), the two conditions (8) and (10) become

$$x_0/i = \rho/\lambda = 2\rho^2/(1+\rho^2), \tag{11}$$

so that $$1+\rho^2 - 2\lambda\rho = 0, \tag{12}^*$$

which gives $$\rho = \lambda - \sqrt{(\lambda^2-1)} \tag{13}$$

(the other sign for the square root would make $\rho > 1$).

If the full normal resistance of the wire is w_0, and the resistance for current i is w, the resistance of the normal region surrounding the core will be $w_0 a^2/(a^2-r_0^2)$, or $w_0/(1-\rho^2)$; thus in order that the electric field should be constant over the cross-section of the wire,

$$w_0(i-x_0)/(1-\rho^2) = wi. \tag{14}$$

Substituting equations (11) and (13), we find

$$w/w_0 = \tfrac{1}{2}\{1+\sqrt{(1-1/\lambda^2)}\}. \tag{15}$$

Thus the resistance should rise discontinuously to half its

* We may note that equation (12), deduced from the condition that the current density should be continuous across the core boundary, can also be deduced from the condition that the Joule heat developed by the current in the whole wire should be a minimum. The Joule heat W, developed per unit time, is wi^2, or using (8) and (14),

$$W = w_0 i\frac{i-x_0}{1-\rho^2} = w_0 i^2\frac{1-\rho/\lambda}{1-\rho^2},$$

and it can easily be seen by differentiating with respect to ρ that the condition for a minimum is indeed just (12).

full value as soon as $i=\frac{1}{2}aH_c$ ($\lambda=1$), and then continue to rise with further increase of current, reaching its full value only asymptotically. In fig. 12*a* we show how the resistance should be restored by a current at constant temperature, according to equation (15). Experimentally, this question is difficult to investigate, on account of the large currents required, since as soon as any resistance is restored a great development of Joule heat occurs, which makes it very difficult to keep a constant temperature. Shubnikov and Alexeevski (7) overcame this difficulty by the ingenious method of immersing the specimen in liquid helium below the λ-point (helium II), which on account of its

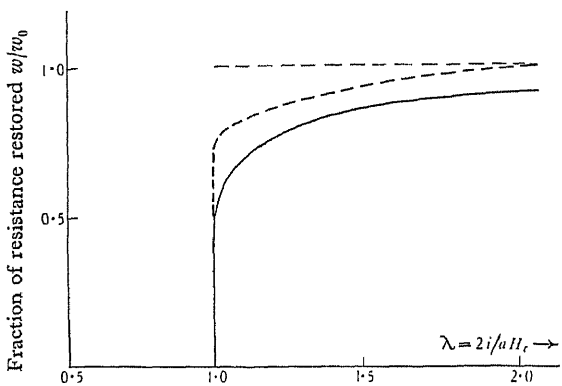

Fig. 12*a*. Restoration of resistance by a current at constant temperature: full curve—theoretical; broken curve—experimental (Shubnikov and Alexeevski (7)).

enormous effective heat conductivity is able to carry away the Joule heat sufficiently rapidly to prevent the temperature from rising. It is interesting to mention that if the same experiment is carried out above the λ-point, as was tried in the original Leiden experiments on destruction of superconductivity by a current, the wire immediately becomes isolated from the liquid by a layer of gas, and the Joule heat is often sufficient to melt the wire, this being accompanied by an explosive boiling of the liquid helium. The experiments of Shubnikov and Alexeevski (the

broken curve in fig. 12*a*) showed that with a monocrystalline wire of pure tin there was indeed a discontinuous restoration of resistance at exactly the current strength predicted by Silsbee's hypothesis, but the discontinuous rise was up to $w/w_0 \doteqdot 0{\cdot}8$, instead of the value 0·5 predicted by the theory. This discontinuous rise was followed by a slower rise, but not as slow as predicted by the theory, and w/w_0 became equal to 1 for a current about twice the critical current, in contrast to the asymptotic approach to unity predicted by the theory.

The cause of these disagreements is not yet clear, but since the experimental conditions seem to exclude the possibility of any

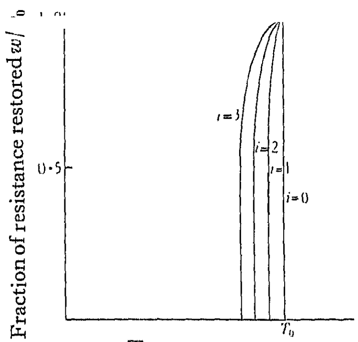

Fig. 12*b*. Influence of current on restoration of resistance (theoretical curve, London (5)).

appreciable temperature rise (the diameter of the wire was only 10^{-2} cm., so that on account of the high thermal conductivity of tin there could not have been any appreciable temperature difference between the inside and the outside of the wire), and since moreover the wire was fairly accurately cylindrical, it is possible that the disagreements may be of a fundamental nature, perhaps similar to the disagreement between the experimental 0·58 and the theoretical 0·50 in the restoration of resistance by a transverse magnetic field (p. 37). Just as there, the theory may perhaps break down on account of the laminae (see below, p. 57) in the intermediate core being too thin (the thickness of the

laminae of fig. 13 decreases with the diameter of the wire), and here again experiments on much thicker wires would be of interest.

Experiments were made also on the destruction of superconductivity by a current in the presence of a magnetic field parallel to the current (7a), and as we should expect, the critical current decreased with increase of the applied magnetic field, vanishing of course when the applied field was equal to H_c. The amount of the discontinuous rise at first fell slightly below 0·8, but for greater fields increased above 0·8, approaching the value unity as the field approached H_c. The presence of a magnetic field greatly complicates the problem of determining theoretically how the resistance should be restored, since the field distribution can no longer be considered in only two dimensions, but some (unpublished) considerations of Landau suggest that the solution will probably involve the mixed state mentioned in Chapter III. If instead of plotting the variation of resistance with current for constant applied magnetic field, the resistance is plotted as a function of field for different constant currents, the curves obtained are qualitatively similar to fig. 12*b*, the abscissae representing field instead of temperature. This has been found also by de Haas and Voogd (8) for the case of the weak measuring currents used in ordinary resistance measurements. The case of destruction of superconductivity by a strong current in the presence of a transverse magnetic field has not yet been investigated experimentally. The theoretical problem is in this case complicated by the absence of circular symmetry in the field distribution, and has also not yet been investigated.

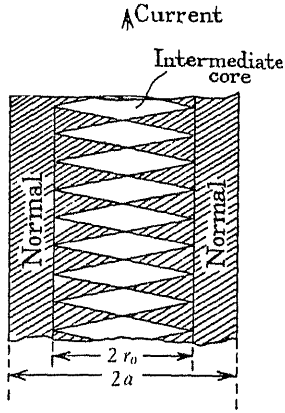

Fig. 13. Destruction of superconductivity of a long cylinder by a current.

The result (15) shows also how the resistance of the wire

should disappear when it is cooled with a constant current i flowing in it; in this case the parameter λ varies in virtue of the variation of H_c with temperature. Above the normal transition temperature T_0, H_c is zero and λ infinite, so that $w = w_0$; as soon as the temperature is reduced below T_0, however, λ becomes finite, and decreases with further reduction of temperature, so that the resistance begins to drop in accordance with equation (15). This continues, however, only until $\lambda = 1$, i.e. until the critical field has reached the value $2i/a$, when the resistance drops abruptly to zero from half its full value and the wire becomes completely superconducting. During the cooling process, the intermediate core appears at temperature T_0, and then grows until, just before the sudden drop of resistance occurs, it occupies the whole of the wire; for any further reduction of temperature, this arrangement becomes unstable, and is replaced by the superconducting state throughout the whole wire.

The variation of resistance with temperature for different currents, as deduced from these considerations, is shown in fig. 12*b* (for the purpose of this diagram it has been assumed that H_c varies linearly with $T_0 - T$, which is true for sufficiently small $T_0 - T$). It will now be understood more precisely why in Chapter I a vanishingly small measuring current was mentioned as one of the conditions for a completely abrupt appearance or disappearance of resistance. Transition curves of the type shown in fig. 12*b* have in fact been observed experimentally by de Haas and Voogd (8), but the currents used were rather too small to allow of more than a qualitative confirmation of the theory.

We have said nothing, so far, about the structure of the metal in the intermediate core, which will evidently be different from that discussed in Chapter III, since here, on account of the current, the lines of force are circular instead of straight. From the expression (9) for the current density inside the core, we see that the intermediate state must consist of a mixture of superconducting and normal regions arranged somewhat on the lines of fig. 13. Thus, since the current density increases towards the

axis as $1/r$, while the electric field is constant, the resistance of a filament at distance r must increase proportionally with r, and so the thickness of the laminae must also vary linearly with r, the normal laminae growing thicker away from the axis, until they fill up the whole length of the wire at the core boundary, the superconducting laminae growing thicker towards the axis. On the axis itself the metal would, according to these considerations, be completely superconducting, but it can easily be seen that a very thin filament round the axis would have to carry only a vanishingly small current, so that there is no contradiction. Just as in the case of an ellipsoid in an external field, the scale of the structure, i.e. the number of laminae per unit length of the wire, will depend on the radius of the core and the surface tension between the superconducting and normal phases. Owing to mathematical difficulties, the number of laminae per unit length cannot be calculated exactly, but its order of magnitude is probably $1/\sqrt{(r_0 d_0)}$. The value of B in the intermediate core varies from H_c at the core boundary to zero on the axis, and it can easily be seen that B at any point in the core is given by

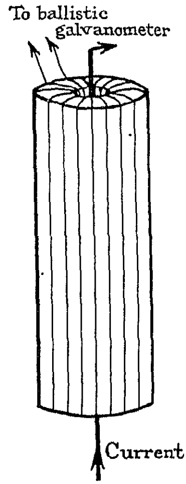

Fig. 14.

$$B=\frac{r}{r_0}H_c. \tag{16}$$

In connection with the question of destruction of superconductivity by a current we may mention an interesting experiment of Stark and Steiner (9). In this experiment a coil, connected to a ballistic galvanometer, was wound round a hollow cylinder in the way shown in fig. 14, so that the lines of force of a current flowing through the substance of the cylinder are embraced by the coil. In their experiment the cylinder was cooled with a current flowing in it, and they observed a sudden deflection of the galvanometer which corresponded to the sudden ejection of all the lines of force from the metal when it became super-

conducting. Thus the deflection of the galvanometer was equal to that obtained by switching off the current when the cylinder was in the normal state. This is the most direct confirmation of the fact that the current becomes entirely superficial when the metal becomes superconducting.* With suitable modifications, the same experimental arrangement could also be used to verify the intermediate stages of the transition to superconductivity, i.e. to show the rearrangement of the field distribution (actually the distribution of B, of course) as the intermediate core grows in the cylinder;† this might provide a more detailed check on the theory than is possible from resistance measurements alone.

* We should mention that this superficiality has also been confirmed by Meissner and Heidenreich (**10**), by studying the field distribution round two neighbouring cylindrical superconductors carrying currents. The field distribution for this case depends on the current distribution inside each cylinder (for a single circular cylinder, of course, the field distribution outside is independent of the current distribution). See also p. 44.

† The hole in the cylinder, however, causes a modification of the structure discussed for the massive cylinder, for, since the field has to vanish at the inside surface of the cylinder, the intermediate state cannot exist there. Landau (**6**) has discussed the problem in detail and finds, that for

$$\tfrac{1}{2} aH_c < i < (a^2 + b^2) H_c/4b \qquad (b \text{ is the radius of the hole}),$$

the mixed state, discussed in Chapter III, has to occur in a region very close to the inner surface, followed by the intermediate state in a core of radius given, as before, by equation (12), and surrounded by the normal state in the rest of the cylinder. For this range of currents, the resistance of the cylinder is given by

$$\frac{w}{w_0} = \tfrac{1}{2}\left[1 + \sqrt{1 - a^2 H_c^2/4i^2}\right]\left(1 - \frac{b^2}{a^2}\right). \qquad (15a)$$

When $i > (a^2 + b^2) H_c/4b$, the intermediate core disappears, but the inner surface of the cylinder is separated from the outer region in the normal state by a small region in the mixed state; for such currents the resistance is given by

$$\frac{w}{w_0} = 1 - \frac{bH_c}{2i}, \qquad (15b)$$

and just as for the full cylinder, w/w_0 approaches unity only asymptotically. In the lower range of currents the value of B in the intermediate core (not too close to the inner surface) is given as for the full cylinder by equation (16); for the higher range of currents, the field at radius r in the cylinder is given by

$$B = \frac{2i}{r}\left(\frac{r^2 - b^2}{a^2 - b^2}\right) + \frac{bH_c}{r}\left(\frac{a^2 - r^2}{a^2 - b^2}\right). \qquad (16a)$$

This equation is of course valid only if r is not close enough to b to fall in the region of the mixed state (i.e. $r - b \gg d_0$); it will be noticed that for very high currents (16a) goes over into the ordinary expression for the field in a hollow cylinder carrying a current, i.e. the second term, which represents the field due to the excess of current flowing in the mixed state, becomes negligible.

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Chapter V

THE THERMODYNAMICS OF SUPERCONDUCTIVITY

The idea of applying thermodynamics to the transition between the superconducting and normal states was originally suggested by Keesom (1) and then by Rutgers (2), and developed in greater detail by Gorter (3), but at that time it was still thought that the transition was essentially irreversible in a magnetic field, since a superconductor was believed to be merely a perfect conductor (in the sense explained in Chapter II), so that the surface currents associated with the field would die away with the production of Joule heat when superconductivity was destroyed by the field. This supposed irreversibility made the validity of Gorter's treatment very doubtful, and it seemed surprising that his results should agree so well with experiment. The reason for this agreement appeared shortly afterwards, with the discovery of the Meissner effect, which showed that the disappearance of the superconducting surface currents in a pure metal is, in fact, not associated with any irreversible energy changes (somewhat analogously to the disappearance of the surface currents in a ferromagnetic when its temperature is raised above the Curie point), and that the basic assumption of reversibility in Gorter's treatment is indeed valid.

The thermodynamics of the superconducting transition in a magnetic field is perfectly analogous to that of any other phase transition, and all the results may be obtained in the simplest possible way by equating the free energies of the two phases. In order to obtain the free energy of the superconducting phase in a magnetic field, it is most convenient to consider a long rod, for then the field at the surface of the superconductor is equal to the

external field. If G_s is the free energy* per unit volume in the absence of a field, then in a field H it becomes $G_s - \frac{1}{2}HI$, on account of the energy of magnetization, $-\frac{1}{2}HI$. Thus, since $I = -H/4\pi$, the free energy is $G_s + H^2/8\pi$; the free energy of the normal state, G_n, is unaffected by the magnetic field, since there is no magnetization in the normal state. As soon as the field becomes equal to H_c, the free energies of the two phases become equal, and the two phases can exist together in equilibrium; for lower fields only the superconducting phase exists, since it corresponds to the lower free energy, while for higher fields only the normal phase can exist. Thus the condition of phase equilibrium is

$$G_n = G_s + H_c^2/8\pi. \tag{1}$$

Although we have deduced this condition by considering only a long rod, it is actually perfectly general. When the body has a non-zero demagnetizing coefficient, the transition of the whole body from superconductivity to normal conductivity is spread over a range of external fields, but, as we saw in Chapter III, during this transition the specimen is divided up into a large number of superconducting and normal regions, and the field at the boundary of any superconducting region is always just H_c throughout the transition. It can be shown by more detailed considerations, into which we need not enter here, that equation (1) is also the phase equilibrium condition between the superconducting and normal regions in a gradual transition of this kind.

We may mention that the mixture of superconducting and normal regions in equilibrium with each other (with a field H_c at the superconducting boundaries) in a body of non-zero demagnetizing coefficient—this is the intermediate state in the case of an ellipsoid—is quite analogous to the mixture of gas and liquid, for instance, which occurs at a certain pressure (which like H_c is a function of temperature) for which the free energies of the gas and liquid are equal. In the case of the liquid-gas

* The free energy concerned here is really the Gibbs free energy, or, as it is often called, the thermodynamic potential.

transition, the relative amounts of the two phases are determined by the total volume of the system, while in the intermediate state of a metal, the relative amounts of the two phases are given by the total induction of the specimen, i.e. by B.

From equation (1) we can deduce the differences of all the thermodynamic quantities for the two phases; thus differentiating with respect to temperature, we obtain the difference between the entropies of the normal and superconducting phases, since $S=-dG/dT$. We find

$$S_n - S_s = -\frac{H_c}{4\pi}\frac{dH_c}{dT}. \tag{2}$$

Since dH_c/dT is always negative, we see that the entropy of the superconducting phase is less than (or equal to, when $H_c=0$) that of the normal phase, or in other words superconductivity corresponds to a more ordered state of the metal. The entropy difference vanishes at the normal transition temperature T_0, i.e. in the absence of a magnetic field, and by Nernst's theorem it must vanish also at absolute zero. The last circumstance means that dH_c/dT must vanish at absolute zero, and this is in agreement with the experimental evidence so far as it goes (the measurements have not, however, been carried down to sufficiently low temperatures to make the confirmation entirely certain). Since the entropy difference vanishes both at $T=T_0$ and at $T=0$, it must pass somewhere through a maximum—this is illustrated by the curves of fig. 17.

From equation (2) we see also that heat is absorbed when superconductivity is destroyed isothermally in a magnetic field, and if the change is made adiabatically, the temperature will drop; we shall discuss the magnitude of this cooling effect later. The heat absorbed in a transition at temperature T of unit volume from the superconducting to the normal state is $Q=T(S_n-S_s)$, or

$$Q = -\frac{TH_c}{4\pi}\frac{dH_c}{dT}. \tag{3}^*$$

* This result was first obtained by Keesom (1) in 1924.

This result is quite analogous to the well-known Clapeyron-Clausius formula, the variables p and V being replaced by $-H_c/4\pi$ and B_c respectively (owing to the linear dependence of magnetization on field in a superconductor, an equivalent replacement is by H_c and $-I_c$). We see that this heat vanishes at the normal transition temperature T_0, since dH_c/dT remains finite at T_0, so that *there is no heat of transition in the absence of a magnetic field*. This has already been mentioned in Chapter I as an experimental fact.

Differentiating equation (2) with respect to T, we find the difference of specific heat per unit volume of the normal and superconducting phases:

$$\Delta c = c_s - c_n = \frac{T}{4\pi} H_c \frac{d^2 H_c}{dT^2} + \frac{T}{4\pi}\left(\frac{dH_c}{dT}\right)^2. \qquad (4)$$

In particular, in the absence of a magnetic field (i.e. for $T = T_0$), we have

$$\Delta c = \frac{T}{4\pi}\left(\frac{dH_c}{dT}\right)^2, \qquad (5)$$

which is known as Rutgers' formula (2), and shows that if the metal is cooled or warmed in the absence of a magnetic field, there will be a discontinuity in its specific heat in passing the threshold temperature. In the absence of a magnetic field, the specific heat of the superconducting phase is evidently always greater than that of the normal phase, but at lower temperatures (i.e. when superconductivity is destroyed in a magnetic field) the sign of $c_s - c_n$ must change, corresponding to the fact that $S_n - S_s$ passes through a maximum. The jump in the specific heat has been found experimentally by Keesom and Kok (4) for tin and thallium (actually a short time before the theory had been developed), and agrees very well with Rutgers' formula, thus confirming the assumption of reversibility at the basis of the thermodynamical treatment.

The formulae (3) and (4) give the heat of transition and specific heat difference for a *complete* transition between the superconducting and normal phases, but, as we have already pointed

out, if the specimen has a non-zero demagnetizing coefficient, this transition is actually spread out over a finite range of *external* fields if at constant temperature (the field at the superconducting boundaries is, however, constant and equal to H_c, throughout the transition), or over a finite range of temperatures if at constant external field (in this case, the field at the superconducting boundaries is also equal to H_c throughout the transition, but this H_c varies with the temperature—the analogy is that of a gas liquefying at varying pressure). Thus if the transition is made at constant temperature with an ellipsoid of demagnetizing coefficient $4\pi n$, the transition will take place gradually as the external field is increased from $(1-n)H_c$ to H_c, and correspondingly, the heat Q of equation (3) will be absorbed gradually. In a similar way equation (4) gives only the difference of the specific heats before the transition began and after it is complete, but says nothing about how the specific heat will vary during the transition. In order to see how the specific heat varies during the transition process, we shall consider how much heat has to be supplied to the ellipsoid to raise its temperature by dT, the external field H being kept constant at a value in the intermediate range. In Chapter III we explained that in the intermediate state we have an intimate mixture of the normal and superconducting phases in proportions x and $1-x$, where

$$x = B/H_c; \tag{6}$$

now owing to the rise of temperature, H_c will decrease slightly and so x will increase slightly, i.e. the proportion of the normal phase will be slightly increased. This transformation of a fraction dx of the specimen from the superconducting to the normal state will, however, require heat $Q\,dx$, so that more heat will have to be supplied to produce the temperature rise than would be required in either of the pure phases alone. In other words, the heat of transition, instead of appearing directly, shows up as an anomaly—obviously an increase—in the specific heat.* If it

* There is some analogy between these considerations and those used in deducing the specific heat of a saturated vapour.

were not for the heat absorbed in the transition, the specific heat in the intermediate state would evidently be $xc_n+(1-x)c_s$ so the specific heat that should actually be observed is

$$c=xc_n+(1-x)\,c_s+Q\,dx/dT. \qquad (7)$$

Substituting the value of x from equation (6), the value of B from Chapter III, i.e. $B=H_c-(H_c-H)/n$, and the value of Q from equation (3), we find for the specific heat of the metal in the intermediate state:

$$c=c_n\left\{1-\frac{1}{n}\left(1-\frac{H}{H_c}\right)\right\}+c_s\left\{\frac{1}{n}\left(1-\frac{H}{H_c}\right)\right\}+\frac{T}{4\pi n}\frac{H}{H_c}\left(\frac{dH_c}{dT}\right)^2. \qquad (8)^*$$

We see, therefore, that at $H=(1-n)\,H_c$ the specific heat will jump upwards from the value c_s to $c_s+\frac{T}{4\pi n}(1-n)\left(\frac{dH_c}{dT}\right)^2$; it will then increase linearly with H until the external field reaches H_c, when it will jump downwards from the value $c_n+\frac{T}{4\pi n}\left(\frac{dH_c}{dT}\right)^2$ to c_n. If, instead of measuring the specific heat, we merely measure the absorption of heat as superconductivity is destroyed by an increasing magnetic field, we shall find that for an increase dH of the external field, heat $Q\,dx$ is absorbed, where dx is the fraction of the metal which has been changed from the superconducting to the normal phase by the increase of field; it is easy to see that this heat is equal to $\frac{T}{4\pi n}\left(\frac{dH_c}{dT}\right)dH$, i.e. that the heat is absorbed uniformly (the quantity for change dH not depending on the value of H). The variation of the specific heat with temperature in a constant external field is also given by equation (8), where now T (and therefore H_c) is the variable instead of H; there will again be two discontinuities at those temperatures for which the constant external field corresponds to $(1-n)\,H_c$ and H_c respectively. It will be noticed that equation (8) predicts infinite discontinuities for the case $n=0$

* This result was first obtained by Peierls (5).

(infinite cylinder or thin disc parallel to the field), but this need not alarm us, since in this case the two discontinuities are infinitely close together, and simply indicate that the whole heat of transition is absorbed at a single field strength or temperature. Since in this limiting case the transition is quite sharp, there is, in fact, no point in applying the considerations for a smeared-out transition, and the formulae (3) and (4) are entirely adequate.

These predictions have not yet been experimentally verified for any ellipsoid, but Keesom and Kok (6) have made measurements of the specific heat of a thallium specimen of irregular shape, in a magnetic field, which provide a qualitative confirmation of the theory.* As we have already pointed out, a specimen of irregular shape has an irregular field distribution round it, and so, unlike an ellipsoid, is unable to enter the intermediate state uniformly at any definite value of the external field. The result of this is in general to make the penetration of the external field into the specimen more gradual, so that the magnetization curve, for instance, has no sharp corner; consequently, the discontinuities of the specific-heat curve are smoothed out, and the transition heat shows up merely as a smooth hump in the specific-heat curve. In fig. 15 we reproduce the experimental curve of Keesom and Kok, together with the curve (shown by the broken line) that we should expect for an ellipsoid comparable with their block (we have assumed $n=0{\cdot}1$). Keesom and Kok pointed out that if the temperature range in which the hump occurs is relatively small (as in the case of fig. 15), it is possible to deduce the total latent heat of the transition from the specific-heat curve. Thus the measurements show that, during the transition, the last term on the right-hand side of equation (7) is rather larger than the other two terms, so that no great error is made by assuming that x varies linearly with the temperature. If this assumption is made, it is evident from

* Owing to a slightly incomplete Meissner effect, more complicated results were obtained if the magnetic field was applied before the specimen had become superconducting. The results quoted apply to a field put on after the specimen had been cooled in zero field.

equation (7) that the transition heat Q will be given by the area of the shaded region in fig. 15 (more precisely, this gives the average of Q over the temperature range concerned); in this way they obtained values of Q in very good agreement with equation (3), thus again confirming the reversibility of the superconducting transition. Alternatively, knowing the value of Q, the value of x at any stage of the transition can be obtained as the ratio of the shaded area, up to the temperature concerned, to Q.* In this

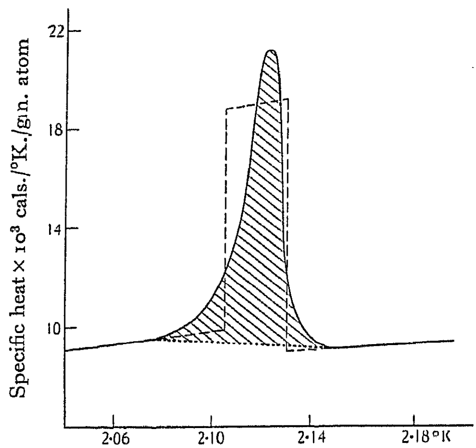

Fig. 15. Specific heat of a thallium block in a magnetic field (33·6 gauss) (Keesom and Kok (6)).

way the curve of fig. 16, showing the variation of x with T, was obtained (the curve for an ellipsoid is shown by the broken line, which is approximately straight on account of the small range of temperatures); we may point out again, that it is because of the rounding off† of the corners of this curve that the discontinuities in the specific-heat curve are smoothed out.

* This is, of course, only a first approximation; a better approximation is obtained if the first approximation is used to correct the assumption (in the first two terms of (7)) that x varies linearly with T.

† The rounding off of the corner at the high temperature end and the similar "tail" in the specific-heat curve (fig. 15) are probably due to slight impurities in the specimen rather than to the irregular shape, for as can be seen from fig. 11, for instance, an irregular shape can usually cause only a gradual beginning of the transition, but not a gradual end.

The detailed form of the temperature variation of the specific heat, and hence of the entropy, has been measured down to 1·2° K. for tin by Keesom and van Laer (4a), and shows the interesting result that the specific heat of the superconducting phase varies approximately as T^3 over practically the whole temperature range in which tin is superconducting. The magnitude of this cubic variation is of much the same order of magnitude as that caused by the lattice vibrations alone, but unfortunately the lattice specific heat at these low temperatures cannot be determined exactly, since even at temperatures high enough for the electronic effects to be negligible, but still low enough compared with the Debye Θ, the lattice specific heat does not vary exactly as T^3.* For this reason, the specific heat of the superconducting electrons cannot be determined by itself; if, however, it can be assumed that below 3·7° K. the lattice specific heat already varies as T^3 (the theory requires that a T^3 variation should set in at some sufficiently low temperature), we can deduce that the specific heat of the electrons in the superconducting state also varies as T^3. Measurements on thallium (4) suggest a similar result (though here the temperature range was more limited, so that the result is less certain), but the question as to whether the T^3 variation is a general property of superconductivity can be settled only by experiments on other superconductors. If the result should indeed prove to be general, it will be of importance in the development of an electronic theory of superconductivity.

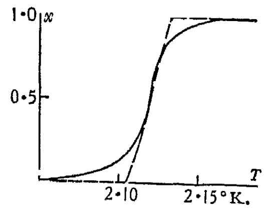

Fig. 16. Temperature variation of x (Keesom and Kok (6)).

Daunt and Mendelssohn (7) have pointed out that, from the purely magnetic measurements, a lower limit can be set to the entropy of the normal state, since evidently the entropy differ-

* For a discussion of this question, see Mott and Jones, *Theory and Properties of Metals and Alloys* (Chapter I), Oxford (1936).

ence between the normal and superconducting states, given by $-\frac{H_c}{4\pi}\frac{dH_c}{dT}$, can never be greater than the entropy of the normal state. From accurate measurements of the H_c-T curves they have constructed the curves of entropy difference against temperature for a number of metals, as shown in fig. 17. The curves suggest that at temperatures low compared with the normal threshold temperature, the entropy difference varies

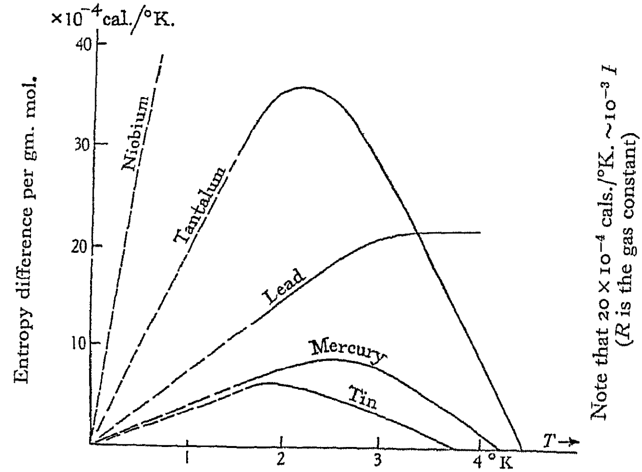

Fig. 17. Entropy difference as a function of temperature for various pure superconductors (Daunt and Mendelssohn (7)).

linearly with temperature (the measurements were not, however, carried down to sufficiently low temperatures to make this conclusion certain), and it may be concluded that the entropy, and hence also the specific heat, of the metal in the normal state also varies linearly at sufficiently low temperatures. From extrapolation of their experimental results Daunt and Mendelssohn obtain the coefficient of the limiting linear variation of the entropy difference with temperature and this is also a lower limit to the coefficient of the linear term in the temperature variation of the specific heat of the metal in the normal state at very low

temperatures. They find that this linear term, which presumably is connected with the electronic specific heat, is in all cases higher (for tantalum and niobium, several times higher) than that predicted by the Sommerfeld formula for an electron gas.* This discrepancy is not surprising, since an electron gas is only a very crude description of a metal, and in any case, the theory on which the formula is based cannot account for the occurrence of superconductivity.

It is important to note that the magnitude of the entropy difference per gm. atom is only about $10^{-3}R$, which is very small compared with the entropy difference for an ordinary transition ($\sim R$),† suggesting either that the rearrangement of the electrons among the various possible states is only very slight, or else that only a very small fraction of the electrons is involved in the superconducting transition. Quite similarly, the energy difference per unit volume between the superconducting and normal phases given by

$$\Delta E = E_n - E_s = \Delta G - T\frac{d\Delta G}{dT}$$

or

$$\Delta E = \frac{H_c^2}{8\pi} - \frac{TH_c}{4\pi}\frac{dH_c}{dT} \tag{9}$$

is of the order of magnitude $10^{-3}RT$ per gm. atom, instead of the order of magnitude RT characteristic of ordinary phase transitions. The energy difference vanishes, of course, at the normal transition temperature T_0.

* Kok(8), assuming that the specific heat of the normal state varied as $aT+cT^3$, while that of the superconducting state varied as γT^3, found the value of a to be in agreement with the Sommerfeld formula for tin and thallium, if the H_c-T curves were assumed parabolic; Daunt and Mendelssohn's measurements show, however, that the latter assumption is only a poor approximation.

† It can easily be seen that if the entropy difference were indeed to be of the order of magnitude R, this would mean a very large entropy for the normal state, and since the entropy has to vanish at $T=0$ there would have to be a very high maximum in the specific heat of the normal phase at some temperature below T_0, just as in the case of a paramagnetic salt (we are supposing that the specific heat of the metal above T_0 has its ordinary low value).

In order to calculate the magnetocaloric effect mentioned on p. 63, it is necessary to know the detailed entropy-temperature curves for the superconducting and normal phases of the metal, and these we have calculated from the specific heat data of Keesom and van Laer (4a) for tin (fig. 18). In this diagram we have inserted the lines of constant external field H for the case of a spherical specimen. As long as the temperature is so low that $H < \frac{2}{3}H_c$, the sphere will be wholly superconducting with

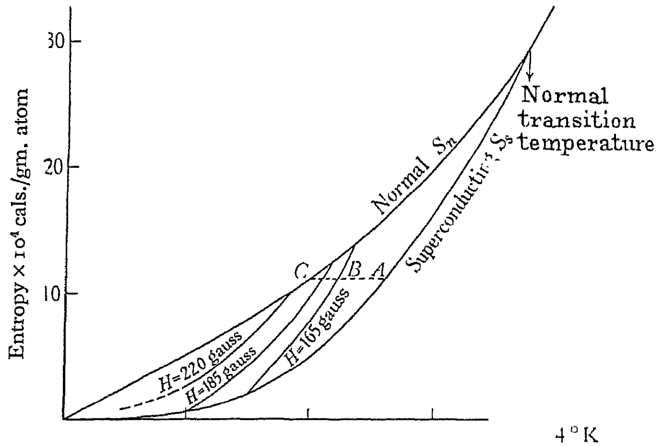

Fig. 18. Entropy diagram for a tin sphere (based on data of Keesom and van Laer (4a)).

entropy S_s given by the lower curve; for $H_c > H > \frac{2}{3}H_c$, the sphere will be in the intermediate state with an entropy $xS_n + (1-x)S_s$, where x, the fraction of the specimen in the normal state, is given by $3H/H_c - 2$, and finally, when $H_c < H$, the specimen will be in the normal state, with entropy S_n given by the upper curve.

With the help of fig. 18, it is easy to deduce the magnetocaloric cooling; thus if the sphere is thermally isolated at temperature A (2·6° K.) and a magnetic field greater than $\frac{2}{3}H_c$, say 165 gauss, is applied, the sphere will have to cool down to B (2·2° K.), in order that its entropy should remain constant. Evidently, for a

given initial temperature, the final temperature will be lowest if the field applied is greater than the critical field at the final temperature reached, e.g. starting from A, the lowest temperature would be C (2·0° K.), which could be obtained by applying a field greater than 210 gauss. We may notice that if the applied field is not greater than the critical field for the final temperature, the latter will be least for a specimen of greater demagnetizing coefficient, since the entropy curve in the intermediate state is then more spread out (to put it another way, more of the specimen will be in the normal state for a given external field than for a specimen of smaller demagnetizing coefficient).

It will be seen from fig. 18 that for tin, starting with the lowest ordinarily available temperature, say 1° K., the lowest temperature that can be obtained by applying a magnetic field is something like 0·1° K. Still lower temperatures could of course be obtained by means of a cyclic process, in which the superconductor cooled down another superconductor, not in a magnetic field, which could then be separated from the first and magnetized, starting already from the lower temperature, and so on.

The idea of using this cooling effect as a method of obtaining very low temperatures was first proposed by Mendelssohn and Moore (9), but although they, and also Keesom and Kok (6), have shown that a lowering of temperature can indeed be obtained, the method has not yet been developed for practical use.* We may mention that it has several disadvantages compared with the Debye-Giauque method of adiabatic demagnetization of paramagnetic salts.

The most serious of these is the very low absolute value of the specific heat of the metal, so that, if it is used to cool down some other substance of comparable or greater specific heat, the drop of temperature produced will be much reduced. This can

* Daunt and Mendelssohn (7) have pointed out that niobium and tantalum might be very suitable substances for the purpose of reaching low temperatures, since the entropy differences for these metals are relatively high (on account of their relatively high critical fields).

be seen at once from fig. 18, for if some other substance of greater specific heat is added to the metal, the entropy curves of the whole system will become much steeper, so that there will be much less difference between the temperatures of the system for which the entropy is the same with the metal superconducting and normal. Thus the method would be useless for cooling down any appreciable amount of liquid helium or paramagnetic salt, and would be inefficient even for cooling down some other non-superconducting metal. Its main use, in fact, would be to cool down the superconductor itself, for the purpose of studying its properties (for instance, the entropy-temperature relation, itself) at low temperatures, and then it has the obvious advantage of requiring only relatively small magnetic fields. We should mention one other feature of the method, which tends to reduce its efficiency; this is that in order to keep the process adiabatic, the magnetic field must be applied infinitely slowly. Indeed, during the cooling process, the specimen is in the intermediate state, so that the change of the field induces eddy currents in the normal regions, whose dying out is accompanied by the irreversible production of Joule heat; consequently, unless the increase of field is made very slowly, the temperature drop produced will be less than that calculated on the assumption of constant entropy.

So far, we have been investigating the thermodynamics of the superconducting transition regarding the pressure p and the volume V of the metal as constants; actually, however, we saw in Chapter I that there is a slight dependence of the critical field on stresses as well as on temperature, and we shall now deduce the thermodynamical consequences of this dependence. We shall deal only with uniform pressures, since owing to the meagreness of the experimental data, there is no point in considering any more complicated stresses.

Differentiating the fundamental equilibrium condition (1) with respect to p, and remembering that $\partial G/\partial p = V$, we find that in a magnetic field there is a change of volume per unit

volume,* given by

$$V_n - V_s = \frac{H_c}{4\pi}\left(\frac{\partial H_c}{\partial p}\right)_T. \qquad (10)$$

If we substitute $-(\partial H_c/\partial T)_p\,(\partial T/\partial p)_{H_c}$ for $(\partial H_c/\partial p)_T$, and remember that $-\frac{TH_c}{4\pi}\left(\frac{\partial H_c}{\partial T}\right)_p$ is just the latent heat Q, we see that equation (10) is just the ordinary Clapeyron-Clausius formula. The only data for $\partial H_c/\partial p$ are those of Sizoo, de Haas and Kamerlingh Onnes (10), for tin and indium, which suggest that $\partial H_c/\partial p$ is of the order of magnitude 10^{-10} abs. unit, so, putting $H_c \sim 100$ gauss, we see that there should be a very minute decrease of volume, of order of magnitude 10^{-9} per unit volume, when superconductivity is destroyed in a magnetic field. McLennan, Allen and Wilhelm (11) have looked for a change of size in a lead rod when its superconductivity was destroyed in a magnetic field, but found no change of length greater than 10^{-8} per unit length, and so presumably there was no volume change greater than $3 \cdot 10^{-8}$ per unit volume; if we suppose that $\partial H_c/\partial p$ for lead is of the same order of magnitude as for tin, this negative experimental result is in agreement with the prediction of equation (10). It should be noticed that, in the absence of a magnetic field, there should be no change of volume at all.

Differentiation of equation (10) with respect to temperature or pressure shows that the thermal expansion and the compressibility should change discontinuously in the superconducting transition even in the absence of a magnetic field. Thus we have

$$\Delta\left(\frac{\partial V}{\partial T}\right) = \frac{\partial V_n}{\partial T} - \frac{\partial V_s}{\partial T} = \frac{1}{4\pi}\frac{\partial H_c}{\partial T}\frac{\partial H_c}{\partial p} + \frac{H_c}{4\pi}\frac{\partial^2 H_c}{\partial p\,\partial T} \qquad (11)$$

and

$$\Delta\left(\frac{\partial V}{\partial p}\right) = \frac{\partial V_n}{\partial p} - \frac{\partial V_s}{\partial p} = \frac{1}{4\pi}\left(\frac{\partial H_c}{\partial p}\right)^2 + \frac{H_c}{4\pi}\frac{\partial^2 H_c}{\partial p^2}. \qquad (12)$$

Since we have no data about the second-order pressure deriva-

* In these formulae, G is of course per constant mass, but since the volume changes are very small, there is no objection to keeping G as per unit volume (strictly speaking G refers to the mass of unit volume in one of the phases only).

tives of H_c, and moreover we are interested only in orders of magnitude, we shall consider only the case when the transition takes place at the normal transition temperature, i.e. when there is no magnetic field present (the orders of magnitude are probably not affected by this limitation). Rewriting (11) and (12) in terms of the coefficient of thermal expansion $\alpha = \frac{1}{V}\frac{\partial V}{dT}$, and the bulk modulus $\kappa = -V\frac{\partial p}{\partial V}$, for the case $H_c = 0$, we find (putting $V = 1$, since all the equations refer to unit volume)

$$\frac{\Delta\alpha}{\alpha} = \frac{1}{4\pi\alpha}\frac{\partial H_c}{\partial T}\frac{\partial H_c}{\partial p}; \quad \frac{\Delta\kappa}{\kappa} = \frac{\kappa}{4\pi}\left(\frac{\partial H_c}{\partial p}\right)^2. \tag{13}^*$$

Putting in rough numerical data ($\partial H_c/\partial p \sim 10^{-10}$, $\partial H_c/\partial T \sim 10^2$, $\alpha \sim 10^{-7}$, $\kappa \sim 10^{12}$), we find

$$\Delta\alpha/\alpha \sim 10^{-2}; \quad \Delta\kappa/\kappa \sim 10^{-9}.$$

The change in compressibility is far too small to observe, and this is confirmed by the negative results of the experiments of de Haas and Kinoshita (12); although the relative change of α is not so small, α itself is so small at the low temperatures at which superconductivity occurs, that the change can be considered as being beyond the limit of observation. In the experiments of McLennan, Allen and Wilhelm (11), in fact, the thermal expansion of lead at the normal transition temperature could only just be detected, so it was impossible to say whether or not there was a discontinuity of the predicted order of magnitude.

* It can easily be seen that these equations are equivalent to Ehrenfest's formulae for a transition of "the second kind" (2), i.e. one in which the entropy and volume do not change.

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Chapter VI

SUPERCONDUCTING ALLOYS

Apart from the pure element superconductors whose properties we have been discussing up to now, there is a great number of alloys which are known to become superconducting at low temperatures (1). Roughly speaking it is possible to divide these alloys into two classes:

(1) Alloys of the superconducting elements either with each other, or with elements which are not at present known to become superconducting and which can become superconducting in a large range of concentrations, so that the superconducting property cannot be said to be characteristic of any particular composition corresponding, for instance, to a chemical compound. There is no universal rule as to how the transition temperature depends on the composition, but in many cases (particularly for addition of bismuth) the transition temperature of the pure superconducting element is increased by the addition of a non-superconducting component (see Appendix, Table III).

(2) Chemical compounds between certain elements (both superconducting and non-superconducting); as examples of this type we may mention Au_2Bi (2) and CuS (3). Although the experimental evidence is rather meagre, it suggests* that the alloys of this type would, if prepared pure (i.e. with exactly the right composition throughout the specimen), behave like pure element superconductors. It seems in fact as if in the case of these alloys the superconductive property is characteristic of the particular arrangement of the atoms corresponding to the lattice of the

* We refer to the low critical field values for Au_2Bi and CuS which are of the same order of magnitude as for a pure metal rather than an alloy of class I. Recent experiments of the author (**3a**) confirm this suggestion; it was shown that if Au_2Bi is suitably prepared its magnetic properties do not differ appreciably from those of a pure element superconductor (i.e. complete Meissner effect).

chemical compound. It is interesting to notice that in all cases of superconducting alloys where neither component is alone superconducting, at least one of the components lies immediately next to one of the two groups of superconducting elements in the periodic system (see Tables I and II, Appendix). This rather confirms the suggestion (Chapter 1) that the grouping in the periodic system is not accidental.

In this chapter we shall be concerned mostly with the properties of the alloys of the first category, which differ in almost every essential respect from those of pure element superconductors. The existence of the other class of alloys may prove to be of importance in the development of a theory of superconductivity, but since it is probable that they do not differ from the simple superconductors in their general properties, we shall not need to discuss them specially. It should therefore be remembered that when in future we use the word alloy, we shall always have in mind alloys of the first kind.

The characteristic difference first found between an alloy and a pure superconductor was in the restoration of the resistance by a magnetic field (de Haas and collaborators (4)). The resistance field curve for an alloy is generally of the type shown in fig. 19, and differs strikingly from that of a pure superconductor. The most striking feature is the very high value of the field required to restore the first trace of resistance; this field varies widely for the different superconducting alloys (we have chosen for the diagram the case of the Pb-Bi eutectic which has one of the highest known critical fields), but is in general some thousands of gauss, instead of the few hundreds of gauss characteristic of most pure element superconductors. Another important feature is that the resistance is restored not in one jump but over a comparatively large range of fields (even if the magnetic field is parallel to the current in the alloy wire). On account of this spreading out of the transition, there is much less difference between the curves for a transverse and a parallel field than there is for a pure superconductor. Alexeevski (4a) has shown that the spreading of the

transition curve in the longitudinal case can be greatly reduced by an increase of the measuring current, and for a current which is still not sufficient to change the mean critical field appreciably, the restoration of resistance is almost as sharp as for a pure metal.

If after the resistance has been completely restored, the magnetic field is again reduced, there is usually a marked hysteresis (see

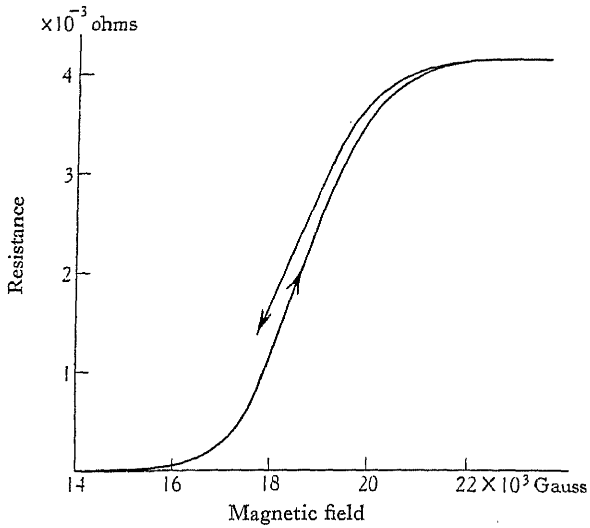

Fig. 19. Restoration of resistance of Pb-Bi eutectic by a magnetic field (4·22° K.) (de Haas and Voogd (4)).

fig. 19; the return curve is not drawn completed owing to lack of experimental data). This hysteresis is presumably connected with the hysteresis in the magnetic properties (i.e. absence of a Meissner effect), which we shall discuss below, but there are very few experimental data available which could allow any conclusions to be drawn as to the more detailed nature of the connection; unfortunately most experiments on alloys have been concerned with some particular aspect, and so there is no alloy for which all the different properties have been studied on one and the same specimen.

The transition temperatures of the superconducting alloys are of much the same order of magnitude as for simple superconductors, but the transition between normal and superconductivity, even in the absence of a magnetic field, is spread over a relatively large temperature range (of order 1° K.). In the literature it is usual to give the transition temperature as that for which the resistance has half its full value, but it should be remembered that this temperature is in general sensitive to the strength of the measuring currents.

Before the magnetic properties were properly investigated, these apparently very high critical fields of alloys suggested several interesting possibilities. For instance, with the use of such an alloy, it seemed that it might be possible to realize the old idea of a superconducting solenoid for fields of a few thousand gauss, since smaller fields, if applied externally, did not restore any trace of resistance. Also if H_c and dH_c/dT were as large as suggested by the resistance measurements, all the caloric effects should appear on a scale several hundred times as large as for pure metals, so that an enormous jump in the specific heat should occur when superconductivity was destroyed in the alloy, and an enormous cooling effect if the destruction was in a magnetic field. In practice, however, it turned out that none of these possibilities could be realized, because the critical field suggested by the resistance measurements is characteristic of only a very small fraction of the bulk of the alloy. We shall now outline briefly the experimental evidence which points to this interpretation.

de Haas and Casimir-Jonker (5), using the bismuth wire technique, showed that actually a magnetic field penetrated into an alloy long before it was large enough to restore the first trace of resistance, and that the penetration was very nearly complete at field strengths of the same order of magnitude as for pure elements. Similarly, Mendelssohn and Moore (6), and Rjabinin and Shubnikov (7), measuring the *B*-*H* curve of a long rod of superconducting alloy, found that *B* ceased to be zero, and

approached the value of H_c at fields much lower than those required to restore the first trace of resistance (fig. 20).* This evidence at once suggests that the real critical field of most of an alloy specimen is of the same order of magnitude as for pure superconductors, but that as the field is increased, a very small fraction of the whole bulk of the specimen, in virtue of a higher critical field, is able to remain superconducting, and so to provide a path of zero resistance for the current used in the resistance measurements.

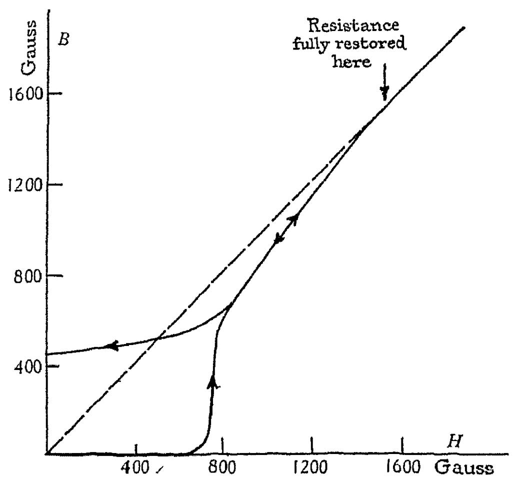

Fig. 20. *B-H* curve for the alloy Pb + 2 % In ($T = 1{\cdot}95°$ K.). (Shubnikov and others (15)).

The failure of the Silsbee hypothesis for alloys also agrees qualitatively with the above interpretation; thus Keesom (8), and Rjabinin and Shubnikov (7), in attempting to make use of an alloy for the production of magnetic fields of a few thousand gauss, found that the resistance of an alloy wire was restored by currents much lower than would produce a field at the surface

* We have chosen a case where the penetration field is not so very much smaller than the field which restores resistance, in order to be able to show all the features in a single diagram. The region of penetration is however often very much greater than that shown in fig. 20.

of the wire of the magnitude of the critical field as determined by resistance measurements. In the experiments of Rjabinin and Shubnikov, it was shown that the field at the surface of the wire produced by the current which first caused a trace of resistance to return was independent of the diameter of the alloy wire, and was of the same order of magnitude (actually about 30 per cent less for the particular alloy concerned) as the field which first penetrated the specimen if applied longitudinally. In terms of the above hypothesis, this probably means that the field of the current which begins to restore the resistance is equal to the lowest critical field of the alloy (supposing that on account of inhomogeneity there is a continuous distribution of critical fields). When this current is exceeded, superconductivity is destroyed in the whole wire in some way similar to that for a pure metal (Chapter IV), except that the process must be complicated by the inhomogeneity of the critical field. The current is unable to flow along the "threads" of high critical field because, presumably, their radii are too small, i.e. roughly speaking because the ratio of the radius of a thread of high critical field to the wire radius is smaller than the ratio of the critical field of the bulk of the wire to the highest critical field. This qualitative explanation of the failure of Silsbee's hypothesis thus suggests that the failure is really only apparent, and that the hypothesis is still qualitatively valid if the critical field is taken not as the field which restores the resistance, but as that which first penetrates the wire, i.e. of the order of magnitude of the critical field of the bulk of the specimen.

Although the explanation given above of the differences between an alloy and a pure superconductor is plausible, it is only very qualitative, and has as yet no theoretical background; so in order to avoid laying too much stress on this particular interpretation, it is convenient to recapitulate the facts from a purely experimental point of view. Thus we can say that in an alloy there are *three* critical fields: (1) the field H_1 produced at the surface of the wire by the current which just restores resist-

ance, (2) the field H_2 at which lines of force first begin to penetrate the specimen, and (3) the field H_3 which is required to restore resistance with only a weak current flowing. The temperature variation of these critical fields is shown in fig. 21 for a particular case.

For a pure metal these three critical fields are identical, but we see that for an alloy H_3 is much larger than H_2, while H_1 is slightly less (in this case by 30 per cent) than H_2. In our interpretation of the failure of Silsbee's hypothesis, we implied that there is really no difference between H_1 and H_2, and indeed it is possible that the field at which the penetration first occurs is really lower than that indicated by Rjabinin and Shubnikov, i.e. that the first penetration was too slight to be detected by their experimental arrangement; it is, however, possible that there is a real difference between H_1 and H_2, and for the time being the question must be left open. The shaded region of fig. 21 is that in which penetration of the external field is becoming more and more complete, but usually the penetration is already very nearly complete soon after H_2 has been exceeded. The field H_3 and the form of the transition curve are, as already mentioned, sensitive to the strength of the measuring current, and, moreover, a considerable increase (of order 50 per cent) of field above H_3 is necessary to restore the resistance completely, H_3 being only the field which restores the first trace of resistance.

Fig. 20 shows another remarkable difference between the properties of an alloy and a pure superconductor, namely, that the Meissner effect does not occur in alloys.* It will be seen, in fact, that there is a very marked hysteresis in the *B-H* curve when the magnetic field is reduced from a value at which it penetrates appreciably into the alloy, most of the flux which had penetrated into the specimen for this field value being "frozen-in". The detailed form of the *B-H* curve depends on the parti-

* It may be noted that on this account the *B-H* curve of an alloy is closer to the theoretical curve for a perfect conductor (fig. 3*b*, Chapter II) than to that for a pure superconductor (fig. 4*b*, Chapter II).

cular alloy and also on the temperature; in contrast to the case of a pure superconductor, the curves for different alloys, or for the same alloy at different temperatures (for similar shapes, of course), cannot be superimposed by a mere change of scale of B and H.*

This absence of a Meissner effect in alloys can also be roughly interpreted in terms of the hypothesis that in alloys there exist regions of abnormally high critical field, if the further hypothesis

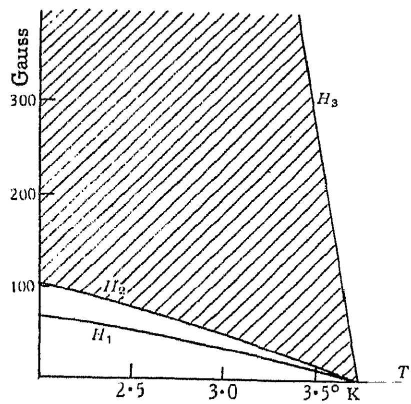

Fig. 21.† Temperature variation of H_1, H_2 and H_3 for the alloy $PbTl_2$ (Rjabinin and Shubnikov (7)).

is made that these regions are multiply connected. Mendelssohn (10) has suggested, in fact, that the structure of an alloy resembles that of a sponge, whose meshes have a much higher critical field than that of the material they enclose. Although

* Some experiments of the author (9) on the magnetic properties of a tantalum specimen (which, presumably on account of impurities, behaved like an alloy) showed that the "freezing-in" was the more complete the lower the temperature was below the normal threshold temperature, i.e. that the hysteresis was more marked at lower temperatures. The more extensive experiments of Shubnikov and his collaborators (15), however, showed that this is not a general rule, since in some cases the hysteresis became *less* marked at lower temperatures. Possibly the difference is due to the fact that the tantalum specimen had a non-zero demagnetizing coefficient, while in Shubnikov's experiments long rods were always used.

† In this diagram H_3 is the field for which the resistance is completely restored, i.e. somewhat higher than the H_3 defined in the text.

this suggestion should be regarded rather as a convenient working model than an established reality, we shall see that it allows a rough qualitative explanation of the observed magnetic properties. As the magnetic field is increased above the value corresponding to the critical field of the bulk of the alloy, it begins to penetrate into the specimen, but the penetration is hampered by the still superconducting meshes of the assumed sponge structure, which tend to keep the flux through the specimen constant. We have seen, however, in Chapter IV, that a multiply connected superconductor is unable to keep the flux constant in the material it encloses when the external field is too much increased, since it cannot carry more than a certain current, and, moreover, this limiting value of the external field is the lower, the thinner the superconducting region. Thus, in spite of the high critical field of the meshes, on account of their thinness, they are not able to prevent the flux through the specimen increasing with the external field, and eventually the penetration of the external field becomes nearly complete, although the meshes (or at least some of them) are still superconducting, and are able to pass a small current without any trace of resistance. When the field is again reduced from some high value, the meshes are at first unable to freeze-in all the flux originally passing through the specimen, since this would require induced currents in the meshes larger than they could carry (again just as in the case of the ring); we have seen in fact that the meshes cannot carry a current higher than that which produces a field at the surface of the wire higher than the critical field of the bulk of the alloy. When the field, however, reaches the critical field of the bulk of the alloy (H_2), the superconducting meshes are able to grow thicker at the expense of the surrounding material, which was formerly in the normal state, but is now in a field less than its critical field. With increase of the thickness of the meshes they are able to carry more current, and thus to prevent most of the flux from leaving the alloy as the external field is reduced to zero; thus eventually the alloy specimen is

left with a large fraction of the flux frozen-in which passed through it when the field had the value H_2 and, moreover, the bulk of its volume (through which this frozen-in flux passes) is left in the normal state.

Further support for the general ideas discussed above is provided by the calorimetric evidence. As we should expect from the evidence already presented, no jump has been found in the specific-heat temperature curve of anything like the order of magnitude originally expected from the critical fields suggested by the resistance measurements (Mendelssohn and Moore (11), Shubnikov and Chotkevitch (12)). This is, of course, because the bulk of the metal has, as we have seen, quite normal critical fields, so that the specific heat of the whole specimen should behave in much the same way as for a pure element. The experiments were designed to look only for the originally expected large jump in the specific heat, and were not sensitive enough to show any small changes in the specific heat; probably a more accurate experiment would show actually not a sharp discontinuity in the specific-heat curve, but merely a hump over the temperature range in which the transition between superconductivity and normal conductivity takes place in the case of an alloy.

The calorimetric method can be used to show that after a sufficiently large magnetic field has been applied and removed from a superconducting alloy (i.e. when the specimen is left with a frozen-in flux), the bulk of the specimen is indeed in the normal state. Thus Mendelssohn and Moore (10) measured the temperature dependence of the specific heat of an impure tin specimen (which as regards the absence of the Meissner effect behaves like an alloy), firstly when it had been cooled in zero magnetic field, and then when a large field had been applied and removed at the lowest temperature. Their results, shown in fig. 22, show that in the second case the specific heat follows the curve corresponding to the normal state without any appreciable discontinuity, i.e. that the frozen-in flux prevents nearly

all of the specimen from becoming superconducting again. With greater sensitivity, this method (which is somewhat analogous to Keesom's method of determining the proportions of normal and superconducting regions during the transition of a pure specimen in a field) might perhaps be used to find how much of the volume of the alloy was occupied by the superconducting meshes, when there was a frozen-in flux in zero field.

Although, on account of the inevitable inhomogeneity of the alloys of the type we have been considering, it is natural that

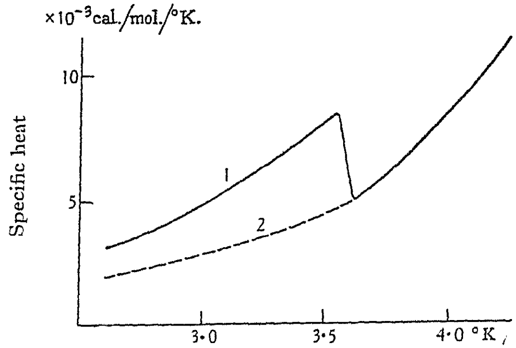

Fig. 22. Temperature variation of the specific heat of the alloy Sn+4 % Bi with (2) and without (1) a "frozen-in" field (Mendelssohn and Moore (**10**)).

they should have a *range* of critical fields (corresponding to the variety of compositions in different parts of the specimen), rather than a single critical field, there is as yet no complete explanation of why some small regions (the meshes of the sponge) should have such abnormally high critical fields as to remain superconducting up to several thousands of gauss. At first sight it might seem that these high critical fields were characteristic of some particular composition which occurred only in very small concentration in the specimens investigated. This idea, however, is unlikely to prove true, for apart from the fact that no evidence has ever been found for the existence of such a high critical field substance in bulk, it is unlikely that

a very high critical field could ever be characteristic of a superconductor in bulk, since its entropy in the normal state (in a magnetic field, of course) would have to be enormously higher than in the superconducting state, and consequently the substance in the normal state would have to have a specific heat much greater than that of an ordinary metal. A more probable hypothesis, suggested by Gorter (13), H. London (**13a**), and Mendelssohn (**13b**, **14**), is that the high critical fields are associated with the small dimensions of the regions which remain superconducting in a high magnetic field (i.e. the meshes of the sponge model). There is in fact evidence that the critical field of a superconductor begins to increase when its size is diminished below 10^{-4} cm. (see Chapter VII) and so it might be supposed that as the magnetic field was increased, the measuring current retired to the regions of the particular composition with the highest H_c (these are the superconducting meshes), these regions being so thin that their critical field was much higher than it would be for bulk material of the same composition. Thus, on this view, the essential difference between an alloy and a pure superconductor lies only in the inhomogeneity of the former, and if an alloy could be prepared with ideally uniform composition, it should behave like a pure metal as regards its superconducting properties; this suggestion is to some extent confirmed by the existence of superconducting alloys of class (2) (see p. 78). More experiments and a deeper theoretical background to the size dependence of critical field (Chapter VII) will be required, however, before this rough interpretation of the anomalous behaviour of superconducting alloys can be made more precise and can be accepted with certainty.

In conclusion we wish to mention one point of practical and historical rather than theoretical interest. This is that the behaviour of alloys described above is in practice nearly always shown to a lesser extent by simple superconductors unless they are extraordinarily pure and free from mechanical strains. A great deal of the experimental work since the discovery of the

Meissner effect has, in fact, been devoted to separating out the properties which we have, in the previous chapters, ascribed to pure superconductors, from the effects caused by minute traces of impurities, and this work has shown that actually very little impurity indeed (less than 10^{-3} per cent solid impurity in some cases) is necessary to produce some of the effects which we have described as characteristic of alloys. Thus in the case of many of the element superconductors, it has not yet been possible to obtain a specimen which shows a complete Meissner effect (i.e. no hysteresis in its magnetization curve), in which the critical field as determined from resistance measurements is not higher than that determined from magnetic measurements, and in which the transition of a long cylinder does not take place over a short range of fields or temperatures, instead of at a single point (a slightly impure element never shows, however, the high critical fields characteristic of alloys).* It is not yet clear which particular impurities are effective in making a superconductor depart from its "ideal" properties; possibly it is dissolved gases (not usually included in purity estimates), or else internal strains, which are responsible for the "non-ideal" behaviour of so many apparently very pure superconductors.

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* We may mention that very pure tin and mercury are the metals which most closely reproduce "ideal" conditions. Tantalum (**14**) and niobium, on the other hand, are examples of metals which behave like alloys even when apparently rather pure.

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Chapter VII

SUPERCONDUCTING THIN FILMS

We have seen that the characteristic property of a superconductor is that $B=0$, and consequently that any current flowing must be superficial. It is, however, obvious that the current cannot be entirely superficial, i.e. that there must be a certain depth of penetration of the current, which will also be the depth of penetration of the magnetic field into the superconductor. Since the $B=0$ description is adequate for specimens of macroscopic size (~ 1 cm.), it is evident that this penetration depth must be very small compared with 1 cm., and we see that effects for which this depth is important can occur only with specimens of very small dimensions. Apart from the possibility of showing effects associated with the penetration depth, experiments with specimens of small dimensions are of interest, since they might give an idea of the minimum size for superconductivity. Just as in the case of ordinary conductivity, superconductivity is a "co-operative" phenomenon, requiring the co-operation of a number of atoms, and so it is natural to expect that there should be a minimum size below which superconductivity could not occur.

There are obvious difficulties in working with specimens which are very small in all their dimensions. So far the only attempt in this direction has been made by Tarr and Wilhelm (1), who investigated the magnetic properties of an emulsion of mercury drops of average diameter 10^{-4} cm. in lard; the experiment showed that B was certainly less than unity for these mercury drops, and that the Meissner effect occurred, but the absolute value of B was not determined, and so the experiment proved only that the penetration depth cannot be much greater than 10^{-4} cm.

Pontius (2) investigated the properties of thin lead wires, and

found that the critical field for return of resistance begins to increase when the diameter of the wire is less than $2 \cdot 10^{-3}$ cm. The law of increase was as $(1 + d_0/r)$, where r is the radius of the wire, and d_0 a constant, and we shall see below that this is in agreement with the theoretical prediction. The increase for the thinnest wire used ($5{\cdot}6 \cdot 10^{-4}$ cm.), however, amounted to only 4 per cent, and the transition to normal conductivity was always spread out, so the results cannot be regarded as entirely convincing from an experimental point of view.

The most extensive experiments which have shown a size dependence of superconducting properties are those with specimens in which only one of the dimensions is small, i.e. thin films. Misener and others (3), working in Toronto with thin films of lead and tin electrolytically deposited on cylindrical metal wires and tubes (usually constantan or german silver), found that the transition temperature of these films began to fall off rapidly below a thickness of order 10^{-4} cm., and that films thinner than about $2 \cdot 10^{-5}$ cm. did not become superconducting at all above 2° K.* We shall see later that this particular result about the size dependence is not confirmed by subsequent experiments, and is probably connected with the method used for obtaining the films, but more interesting are the magnetic properties of these films, which are probably caused by a genuine size effect since they have been confirmed by subsequent experiments using an entirely different method (see below).

It was found that just as for alloys there were three different critical magnetic fields for these films (only the tin films were investigated completely). These were:

(1) The field h_1 produced by the current necessary to restore the first trace of resistance. This was much lower than the critical field H_c for massive tin—about 30 per cent of H_c for the thickest film used ($12 \cdot 10^{-4}$ cm.), and about 3 per cent of H_c for the thinnest ($3 \cdot 10^{-5}$ cm.); there was no simple relation between the field

* The results for lead and tin differed only in detail, the order of magnitude of the critical thickness being the same for both.

h_1 and the film thickness. Unlike a pure metal in bulk, these films showed no discontinuity in the restoration of resistance by a current, the return of resistance being spread over a large range of currents. It was verified that the current to restore resistance was proportional to the radius of the cylinder on which the film was deposited for films of equal thickness, so that it is justifiable to associate the restoration with the magnetic field of the current at the surface of the film.

(2) If a magnetic field was applied transversely to a tube on which the film was deposited, no penetration of lines of force through the tube took place until the external field reached a critical value h_2. For further increase of the external field, however, the penetration became complete only very gradually, and even at fields more than 40 times h_2, penetration was only 99 per cent complete. The magnitude of h_2 was usually several times larger than that of h_1, but always less than H_c for massive tin. It is easy to see that if there were no size dependence, h_2 should be equal to $\frac{1}{2}H_c$, and this was roughly true for the thickest film ($12 \cdot 10^{-4}$ cm.), although penetration was not complete even at $10H_c$; for one of the thinnest films ($6 \cdot 10^{-5}$ cm.) h_2 was of the order of 30 per cent of H_c. These results are very reminiscent of the penetration of a field into an alloy, but unlike the case of an alloy, there was no hysteresis when the field was reduced, i.e. no field could be frozen in the tube.

(3) The field h_3 which restored the first trace of resistance was larger than the critical field of massive tin, just as would be the case with a massive specimen to which impurity was added, but in contrast to the behaviour of impure tin, a greater field was required transverse to the direction of the measuring current than parallel to it. In all cases the return of resistance appeared to be spread over a range of fields comparable with h_3 itself, and since h_3 was not very much greater than H_c for massive tin, it would seem that the resistance had completely returned before the magnetic field had completely penetrated the film; it is probable, however, that this feature is merely due to an insuffi-

ciently precise determination of the field for which the resistance was completely restored. This explanation is, indeed, rendered plausible by the fact that, as soon as any appreciable resistance of the film is restored, the resistance of the metal backing is much smaller than the resistance of the film, so that the measured resistance is mostly that of the metal backing, and any incompleteness of the return of the film resistance would be very difficult to detect. Thus the results are not inconsistent with the hypothesis that the return of resistance and penetration of the field through the film become complete together, as in an alloy, at fields much higher than H_c. The values of h_3 did not appear to depend very much on thickness, but, just as in an alloy, were very sensitive to the strength of the measuring current, h_3 decreasing with increase of current. The resistance-field curves always showed a marked hysteresis, again as in an alloy.

It will be seen that the behaviour of these electrolytically deposited films is in many ways similar to that of alloys, and so it seemed possible that some of the anomalies might indeed be due to alloy formation between the film and the metal backing at their surface of contact. It was found that if a layer of non-superconducting metal such as copper was deposited on top of the superconducting film, the film assumed properties corresponding to a much thinner film without a covering layer—the transition temperature, for instance, began to fall off with thickness for much thicker films if they were covered with a copper film, than if they were not (about 10 times thicker). If the falling off of transition temperature is indeed due to alloying, this last result would be quite natural, since in the copper-covered films there are two surfaces instead of one, at which alloying could take place. Alloying cannot, however, explain why the critical fields h_1 and h_2 are so much smaller than for massive tin, and this feature is no doubt a genuine size effect.

In order to eliminate the possibility of complications due to alloying, Shalnikov (4) has made experiments with very thin tin and lead films deposited on glass at 4·2° K. by evaporation in very

rigorous conditions of cleanliness. So far only preliminary results are available, but these are already of great interest, and seem to confirm our view that the effects observed by Misener are only in part due to a size dependence. First of all, Shalnikov has found that films of lead and tin as thin as $5 \cdot 10^{-7}$ cm. become completely superconducting; the transition temperature of the tin films was about $4{\cdot}7^\circ$ K. (i.e. 1° K. higher than for the bulk metal), while for the lead films, although the transition temperature could not be determined exactly, it also seemed to be appreciably higher than for the bulk metal. It thus appears, in contrast to the result of Misener, that superconductivity can still exist even for a film of only 15 atomic layers.

For technical reasons Shalnikov has as yet only worked with films deposited on a plane surface, so his results on destruction of superconductivity by a current are not so simple to interpret in terms of the magnetic field of the current as are those of Misener on cylindrical films. It was found that superconductivity was destroyed by very low currents, e.g. 2 milliamperes for a lead film $5 \cdot 10^{-7}$ cm. thick and 3 mm. wide at $4{\cdot}2^\circ$ K. A rough calculation shows that the maximum field produced by this current at the surface of the film—this will be at the edge of the film—is only about 10 gauss, which is only about 2 per cent of the ordinary critical field of lead. The critical current increases with thickness of the film, but in rather a complicated way. An important feature of the results is that the resistance returns very abruptly, there being only a very slight further increase of resistance for increase of the current above the critical value—this again contrasts with the smeared-out transitions found by Misener, and suggests that the smearing out was not a feature caused by the reduction of size, but of secondary origin. Qualitatively we may say that Shalnikov's work confirms the result that the critical field h_1 for a current is much smaller than the critical field for the massive metal.

Perhaps the most remarkable property of the evaporated films is the great magnitude of the external magnetic field (either

transverse or parallel) which has to be applied to the film to restore its resistance. The magnetic field necessary to restore the resistance decreases with increase of the measuring current, and by rough extrapolation to zero current, the field h_3 was estimated to be 15,000 gauss for a lead film $6 \cdot 10^{-6}$ cm. thick, while for the thinnest films, although no reliable extrapolation could be made, it was evident that h_3 was much higher still. The question of penetration of magnetic fields into the films has not yet been studied, so it is not yet possible to say whether these films have an h_2 value different from h_1 or h_3.

All the properties described above were obtained with films deposited at 4·2° K.; if the film was subsequently warmed to room temperature, and then again cooled, it could be seen that a marked annealing had taken place, the normal resistance being much smaller than originally. This annealing had a marked effect also on the superconducting properties: in the case of the tin films, the transition temperature dropped from its abnormally high value to about 3·7° K. (that of the bulk metal), and for all the films the other anomalous properties became less pronounced. Thus the critical currents became rather higher and the fields h_3 a good deal smaller (in one case h_3 fell to only 2 or 3 times H_c, the critical field of the bulk metal); they were, however, still considerably different from the values of the bulk metal, and so we can say that the *qualitative* features of the superconducting properties were not changed by the annealing. Although it is evident that Shalnikov's results are in part due to the structure of the films (which, presumably, is modified by annealing), it is likely that they are at least to some extent also due to the thinness of the films; experiments now in progress, in which different deposition temperatures and annealing conditions are being tried, should help to make the position clearer.

It will be seen that a great deal more experimental work on thin films has yet to be done to make their properties clear, but taking Misener's and Shalnikov's results together, we can say that the following facts are already fairly definitely established:

(1) That superconductivity can occur in films of only 15 atomic layers thick.

(2) That just as in alloys, there are different critical fields for return of resistance caused by a current, for penetration of a magnetic field, and for return of resistance caused by an external magnetic field. In particular, the critical field for restoration of resistance by a current, i.e. the surface density of the critical current, is much smaller than for a massive superconductor, while the field h_3 is much higher than for a massive superconductor.

We now have to consider how far the size dependence of superconducting properties can be interpreted theoretically. Since we know nothing about the mechanism which keeps the magnetic field out of the interior of a superconductor, nothing can be said *a priori* about the conditions in the surface layer into which the field penetrates, so that no detailed theory can be developed without special assumptions. H. London (5), using the special assumptions of the theory of F. and H. London (6), has indeed shown how a low h_1 and a high h_3 can be explained, but since we consider the basic assumptions of the theory to be arbitrary we shall not give any details beyond this reference.

It is however possible to make some general theoretical deductions without any special assumptions. Pomerantchuk (7) has in fact pointed out that it is possible to deduce the size dependence of h_3 from general considerations if the sizes are still fairly large compared with the penetration depth. In this case the conditions in the surface layer can be treated "summarily", by introducing the coefficients of surface tension α_s and α_n of the superconducting and normal phases. Thus equation (1) of Chapter V (which of course neglects surface effects) becomes modified by taking into account the surface energies of the two phases. For the case of a long cylinder or a thin plate parallel to the magnetic field, the free energies of the two phases become equal for a field h given by the equilibrium condition:

$$G_n + \alpha_n A/V = G_s + h^2/8\pi + \alpha_s A/V, \qquad (1)$$

where A and V are the surface area and volume of the specimen. Now $G_n - G_s = H_c^2/8\pi$, where H_c is the critical field for a massive specimen, and $A/V = 2/r$, where r is the radius of the cylinder or the thickness of the plate, so we have

$$h = H_c\{1 + 16\pi(\alpha_n - \alpha_s)/rH_c^2\}^{\frac{1}{2}} \tag{2}$$

or for sufficiently small values of $h - H_c$

$$h = H_c\{1 + 8\pi(\alpha_n - \alpha_s)/rH_c^2\}. \qquad (3)^*$$

This size dependence is of the same type as that found experimentally by Pontius, and numerical agreement is obtained if $\alpha = \alpha_n - \alpha_s$ is put equal to 0·1 erg/cm.^{2}. Since the two phases "wet" each other, α is evidently just the coefficient of surface tension between the superconducting and normal phases, as introduced in Chapter III. The quantity $8\pi\alpha/H_c^2$ has the dimensions of a length and is evidently of the order of magnitude of the penetration depth d_0 (a similar result was obtained in Chapter III, p. 34). Substituting the value of α just found, we obtain $d_0 \sim 10^{-5}$ cm.

The result (2) is valid only as long as $r \gg d_0$ (this condition was fulfilled in Pontius' work), since for smaller r, the division of the energy into a volume and a surface part is no longer possible, and it is necessary to know the detailed conditions in the surface layer into which the field penetrates. Since, however, the formula for the initial behaviour shows an increase of h with decrease of r, it is probable that this increase continues for smaller r, and so we may say that the high h_3 values found experimentally for thin films are theoretically reasonable. It should be noticed that on these views there should be no difference between the field h_3 and the field h_2 (defined as the

* von Laue (8), on the basis of the Londons' theory, obtains a formula of the same type: $h = H_c(1 + \sqrt{\Lambda c^2}/r)^{\frac{1}{2}}$ (this is for a wire), where Λ is the fundamental parameter of the Londons' theory, and $(\Lambda c^2)^{\frac{1}{2}}$ is the order of magnitude of the penetration depth. A similar formula with a minus sign in the bracket gives also h_1, the critical field for destruction by a current. These formulae are of course only first approximations, valid for $r \gg d_0$.

value of the field which penetrates completely into the interior of the specimen).

The question of how h_1 should vary with r is more difficult, since in this case the transition does not become complete when the current exceeds the critical value (owing to the formation of a core in the intermediate state—see Chapter IV) but the fact that h_1 becomes less than with H_c for small r is also reasonable on general grounds. Thus, as the radius of the wire is reduced, the area of the cross-section of the wire occupied by the current flow is at first proportional to r, the penetration depth being constant; as soon, however, as r becomes comparable with or less than d_0, it is evident that this area must fall off more rapidly than r, and so the wire will not be able to remain superconducting for as large values of $2i/r$ $(=h_1)$ as when $r \gg d_0$. This argument* is of course very rough, and can be made more precise only by more detailed knowledge of the current distribution in the surface layer (such as is assumed for instance in the Londons' theory), but it is sufficient to make the decrease of h_1 with size understandable.

It will be seen that one of the most important problems to be solved is the determination of how the field and current are distributed inside a superconductor of small dimensions. On the one hand this knowledge would permit correlation of the various experimental results, and on the other it might give the clue to the theoretical interpretation of the zero permeability of a massive superconductor. The problem could probably be solved inductively from an exact knowledge of the size variation of h_1 and h_3, but the technical difficulty here is to obtain specimens of widely varying sizes with the

* It should be noticed, however, that the argument implies the plausible assumption that the determining factor in the destruction of superconductivity is the local current density in the specimen. This is evidently justified for a massive specimen, for it is then equivalent to saying that the determining factor is the field at the surface. Whether it is true for small specimens is not known, but it is at least plausible, and as is shown above leads to qualitatively correct conclusions.

same atomic structure, i.e. to eliminate effects other than those due to size. A direct measurement of the magnetic moments of small superconductors would also give a partial solution (an integrated form of the distribution), but so far the obvious experimental difficulties have not been overcome.

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Note added in proof. Appleyard and Misener (*Nature*, **142**, 474 (1938)) have just published results of experiments on evaporated mercury films which confirm a number of features of Shalnikov's results.

Chapter VIII

CONCLUSION

In this concluding chapter we shall sum up briefly the results of this survey of superconductivity.

It appears that the essential feature of a pure massive superconductor is that a magnetic field cannot enter into it deeper than a very small penetration depth, i.e. that a superconductor of macroscopic dimensions has zero permeability. As a consequence of this it follows that a superconductor can carry a current on its surface without the aid of an electric field, so that it behaves as if it has zero resistance.

A great deal of the recent work has been concerned with the investigation of the process of transition between super and normal conductivity caused by a magnetic field, and has led to the idea of an intermediate state which is a special kind of intimate mixture of the superconducting and normal phases. With the help of this idea, most of the features of the transition can—in simple cases at least—be fairly well explained, but there still remain some obscure features as regards the electrical resistance of the metal in the intermediate state. These are probably connected with the fact that at the boundary of the specimen the division into superconducting and normal regions becomes so fine that the two phases lose their separate identity and we have a kind of mixed phase, whose properties are not as yet understood. The investigation of the mixed phase and of the size of the laminae in the intermediate state are the main problems connected with the transition in a magnetic field which have yet to be cleared up. Apart from these two problems, which are closely connected with the properties of superconductors of small dimensions, we can say that the explanation of the transition process follows from the zero permeability property of a

superconductor, and requires no deeper theory of the origin of this property.

Similarly, the application of thermodynamics to the superconducting transition has shown that the jump in the specific heat, the latent heat of transition which vanishes in the absence of a magnetic field, and the more complicated caloric properties of specimens which distort the external field, are all consequences of the magnetic properties of the superconductor. Also from the slight pressure dependence of the critical field we have seen why it is that the volume change, and the changes of thermal expansion and elastic properties in the superconducting transition, are so small as to be beyond the limit of observation.

When we come to superconducting alloys the position is no longer so clear; on general grounds it would seem unlikely that there should be two different kinds of superconductivity, and so it is natural to try to explain the anomalous behaviour of alloys as due to some subsidiary cause, such as the inhomogeneity of composition. It does indeed seem possible to account roughly for the smearing out and irreversibility of the superconducting transition in alloys, and for the existence of different critical fields for destruction of superconductivity by a current and an external magnetic field and for penetration by a field, by supposing that the alloy is a mixture of superconductors of different critical fields, but individually all having the properties of a pure superconductor. The fact that the critical field for restoration of resistance is so much higher than the other two can be roughly explained as due to the small dimensions of the regions which carry the superconducting current, but this explanation is only very rough, and may have to be revised.

The properties of superconductors of size comparable with or less than the penetration depth of a magnetic field, so far studied mainly in the form of thin films, can evidently not be explained in terms of the zero permeability property of massive superconductors, since this property is possessed only when the penetration depth can be neglected. The further investigation

of size effects is thus likely to be a particularly profitable line of research, since it may provide the basis for a deeper theory of superconductivity, i.e. explain the origin of the zero permeability of a massive superconductor, and this in turn would be a great step forward towards the interpretation of superconductivity in terms of the electrons in the metal. The analogy between the properties of superconducting thin films, as at present known, and the properties of alloys, suggests, as we have seen, that they may be connected, and so an explanation of the former might also lead to a more precise explanation of the latter.

The discovery of the reversibility of the magnetic properties, and the validity of the thermodynamical consequences of these properties, have made it clear that the superconducting transition is just an ordinary phase transition (a transition of the "second kind," in the absence of a magnetic field), and the fact pointed out in Chapter I, that many properties of the metal are so little different in the normal and superconducting phases, finds its explanation in the low temperature at which the transition occurs. By analogy with other phase transitions we might expect, in fact, that only properties connected with processes involving energies comparable with or less than kT could be appreciably different in the two phases, if T is the temperature of the transition. Thus, for instance, the energy of a light quantum in the visible range is of the order $10^4\, kT$, so we could hardly expect there to be any appreciable difference in reflection or absorption of visible light as between the superconducting and normal phases. For ordinary low-frequency electromagnetic waves there is no absorption in the superconducting phase, and so it is reasonable to expect that there should be a critical frequency of order of magnitude kT/h, at which absorption should begin to occur. This corresponds to a wave-length of about 1 cm., which unfortunately is technically rather difficult to obtain; at present the only experimental evidence is that the critical wave-length is above 10^{-2} cm. and below 10^3 cm., which is in agreement with the above considerations.

There is as yet no electronic theory of superconductivity: essentially the difficulty is that the present electronic theory of metals treats the electrons as if they behaved like a gas, and since it is well known that there can be no phase transitions in a gas, it is not surprising that this theory cannot account for the occurrence of superconductivity. In fact, we can hope for an electronic theory of superconductivity only when methods have been developed for taking account of the strong interaction forces between the metallic electrons. Such a theory would explain the thermal conduction properties of superconductors, and also the temperature variation of the specific heat, but probably a preliminary, more phenomenological theory will first have to be developed. Just as in the theory of ferromagnetism the magnetic properties were first explained in terms of magnetized domains, and only later the reason for this magnetization was explained in terms of the electrons, so here, too, it is likely that there will be a first stage* which will provide a mechanism for the zero permeability, before an electronic theory is developed.

* A useful contribution to this first stage has just been made by Kikoin and Goobar (*C.R. Acad. Sci. U.R.S.S.* **19**, 249 (1938)), who have measured the gyromagnetic effect in superconductors (by means of a resonance method). They found that the ratio of the magnetic moment to the angular momentum is just $e/2mc$ (i.e. Landé's g-factor equals unity), and this suggests that the surface currents which keep the field out of a superconductor are ordinary electron currents, and are not for instance in any way connected with electron spin.

The elements enclosed in rectangles become superconducting at the temperatures shown, and the type of crystal symmetry is also indicated. For the other elements the figure in brackets gives the lowest temperature at which the element has been investigated and found not superconducting. The small figures are references to literature.

																He
											B (1·27)	C (1·15°)	N	O	F	Ne
											Al 1·14° cub. f.c. (15)	Si (1·22°)	P (2·8°)	S	Cl	Ar
Sc		Ti 1·81° hex (28) (33)	V 4·3° cub. b.c. (36)	Cr (1·41°)	Mn (1·22°)	Fe (0·75°)	Co (1·36°)	Ni (0·75°)	Cu (0·05°)	Zn 0·79° hex (16)	Ga 1·07° rhomb. (11)	Ge (0·05°)	As (1·13°)	Se (1·26°)	Br	Kr
Y		Zr 0·70° hex. (38)	Nb 9·22° cub. b.c. (29) (35)	Mo (1·26°)	Ma	Ru (1·17°)	Rh (1·32°)	Pd (1·17°)	Ag (0·74°)	Cd 0·54° hex. (38)	In 3·37° tetr. f.c. (4)	Sn 3·69° tetr. (2)	Sb (1·16°)	Te (1·13°)	I	X
La 4·71° hex (40)	Rare Earths	Hf 0·35° hex. (33)	Ta 4·38° cub. b.c. (25)	W (0·74°)	Re (1·36°)	Os (1·8°)	Ir (1·29°)	Pt (0·77°)	Au (0·05°)	Hg 4·12° rhomb. (1)	Tl 2·38° hex. (3)	Pb 7·26° cub. b.c. (2)	Bi (0·05°)	Po	—	Rn
Ac		Th 1·32° cub. b.c. (28) (42)	Pa	U (2·2°)												

the necessary data was available and the correction was appreciable, the threshold temperatures given by the original authors have accordance with the 1937 Leiden helium vapour pressure curve (see Schmidt and Keesom, *Physica*, 4, 971 (1937)). For the right-uperconductors the accuracy of the temperatures given is probably of the order 0·02° K., but for the left-hand group there are iderable differences between different specimens of the same element (e.g. Ti: 1·20° K. (28) and 1·81° K. (33); Th: 1·49° K. (28) 2)). In such doubtful cases we have given the figures which seem to correspond to the purest specimens, but most of the figures d group of superconductors should be regarded as indicating only the orders of magnitude of the threshold temperatures.

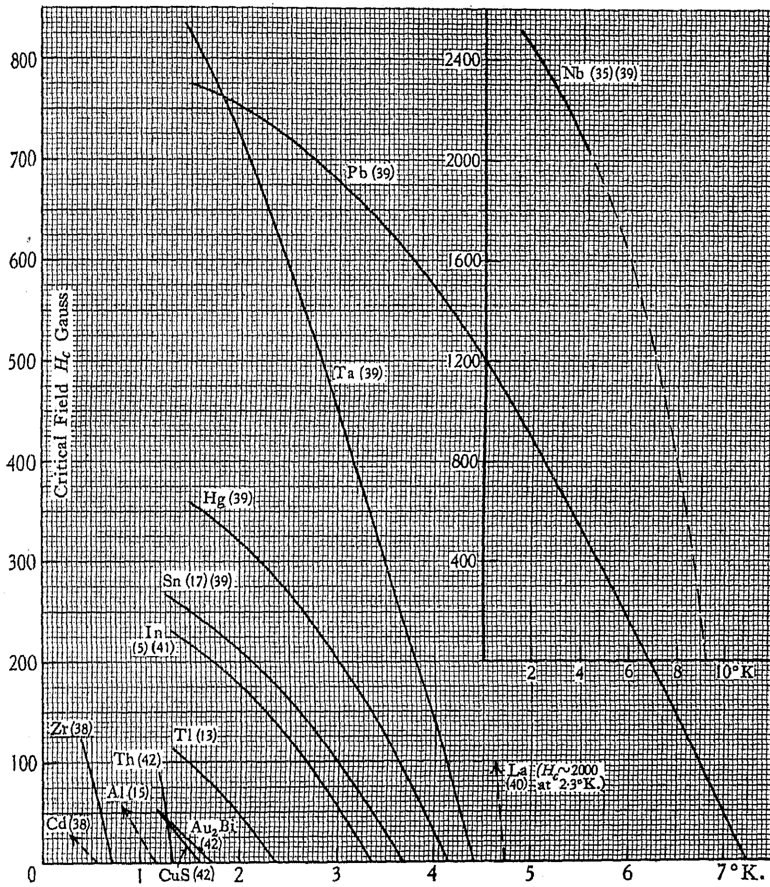

Fig. 23. H_c-T curves. (The bracketed figures give references to the literature.)

This diagram contains all the most reliable data available at the time of writing. The broken curve for Nb is a guessed interpolation between the normal transition temperature and the highest temperature at which H_c has been measured. The curves for Hg, Nb, Pb, Sn, Ta, Th, Zr, Au_2Bi, and CuS are based on magnetic measurements, while those of In and Tl are based on resistance measurements. For Al, Cd and La only the orders of magnitude of the initial slopes are known (for Al from the destruction of superconductivity by a current), and these are indicated by the arrows. Probably the most reliable curves are those for Hg, In, Nb, Pb, Sn and Zr

TABLE II. SUPERCONDUCTING COMPOUNDS

Name	Transition temp. ° K.	Remarks and Literature
Pb_2Au	7·0	(9) (21)
$PbTl_2$	3·8	High H_c (see fig. 21) (9) (12) (
Pb_5Na_2	7·2	(19)
SnSb	3·9	(6)
Sn_3Sb_2	4·0	$H_c = 134$ at 3·58° K. (6) (12
Sn_2Au	2·5–2·75	(23)
Sn_4Au	2·5–2·75	(23)
Tl_3Bi_5	6·4	$H_c = 4000$ at 4·2° K. (6) (10) (12
Tl_2Hg_5	3·8	(9)
Tl_7Sb_2	5·2	(9) (21)
Au_2Bi	1·7	For H_c see fig. 23 (7) (12) (42
CuS	1·6	For H_c see fig. 23 (27) (42)
TaSi	4·4	(31)
MoC	7·6–8·3	(30) (35)
Mo_2C	2·4–3·2	(30)
NbC	10·1–10·5	(30)
TaC	9·3–9·5	(30)
TiC	1·1?	(30)
WC	2·5–4·2	(30)
W_2C	2·0–3·5	(22)
ZrC	2·3	(31)
TiN	1·2 and 5·5	Two jumps (30) (31)
VN	1·5–3·2	(30)
ZrN	9·3–9·6	(30) (31)
ZrB	2·8–3·2	(31)

Only in a few cases (e.g. Au_2Bi and CuS) is it certain that the figu definitely to the compound listed, of homogeneous composition th the specimen. In some cases (e.g. $PbTl_2$ and Sn_3Sb_2) there is dou existence of the compound or doubt as to its homogeneous composi for instance Hansen, *Der Aufbau der Zweistofflegierungen*, Springer and in others (e.g. Pb_5Na_2) it is possible that superconductivity i excess of one of the components in the free state, rather than to the co listed. The fact that the superconducting transition is often spread o only a single temperature is given it must not, however, be assumed transition is sharp), and the high H_c values of some of the compou be due to these causes, which would indicate that they belong to T rather than to Table II. In the case of some of the carbides, nitri the superconducting properties vary considerably among different s —we give the data for the specimens with the sharpest transitions.

TABLE III. Superconducting alloy series

Other component	Pb	Sn	Tl
Ag	5·8–7·3 (8) (9) (21) (24)	3·3–3·7 (23) (24)	(E) 2·7 (9) (23) ?(35)
As	(E) 8·4 (21) ? (35)	(E) 4·1 (21)	
Au	2·0–7·3 (9) (21) (24)	2·6–3·7 (9) (23) (24)	(E) 1·9 (8)
Bi	7·3–8·8 (12) (20) (34) High H_c for all compositions; (E) 8·8: very high H_c (fig. 19)	(E) 3·8 (8) (10) $H_c = 130$ at 3·48° K.	
Ca	7·0 (21)		
Cd	7·0 (8) (18) (37) ?(35)	(E) 3·6 (8) (10) $H_c = 266$ at 1·98° K.	(E) 2·5 (8) ?(35)
Cu	7·3–7·8 (24)	3·6–3·7 (24)	
Hg	4·1–7·3 (32) For 15 % Hg $H_c = 6800$ at 4·2° K.	>4·2 (2)	
In	3·4–7·3 (32) (37) For 8 % In $H_c = 2400$ at 4·2° K.		2·4–3·7 (32)
Li	(E) 7·2 (21)		
P	(E) 7·8 (21)		
Sb	(E) 6·6 (8) (20)		
Tl	2·2–7·3 (12) (34) For 30 % Tl $H_c = 3000$ at 4·2° K. (37)	2·4–6·2 (24) (32)	

Hg-Cd 1·7–4·1. For 5 and 10% Cd, H_c approx. same as for pure Hg (14) (18) (37); Mo-C 1·2–8·9 (32) (35).

Some superconducting alloys with more than two components are: Rose's m[illegible] [illegible]'s metal (8·5) (20), Wood's metal (8·2) (20). PbAsBi: (9·0) (21). PbAsBiSb: (9·0) (21). All these have high H_c.

The temperature range given is usually that of the temperature at which half the resistance disappears (in a few cases, that at which the whole resistance disappears), for different alloys of the given series. Since the resistance disappears over a temperature interval sometimes as large as 2° K., which depends on the strength of the measuring current and the heat treatment of the alloy (details of these are not always to be found in the original papers), the figures given are necessarily rough. The letter *E* in front of a figure indicates that this is the mean transition temperature of the eutectic—apart from this, the table gives no indication of the type or structure of the various alloys; such information can sometimes be found in the original papers, which should be consulted in conjunction with the equilibrium diagrams of the alloy systems (see for instance Hansen, *Der Aufbau der* [illegible] Springer (1936)). A query in front of a reference number indicates that the work referred to questions the data given; thus in some cases, it is likely that superconductivity is due to one of the components in the free state (e.g. Pb in the Pb-Cd series)—there are probably many more such cases than indicated by the query marks. The H_c values given are the field strengths at which half the resistance (in some cases the whole resistance) is restored, and are meant to serve only as a guide to the orders of magnitude; more detailed data can in some cases be found in the original papers.

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